(12) **EUROPEAN PATENT APPLICATION**

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(54) Optical device including birefringent polymer.

(57) Optical devices including a molecularly oriented highly birefringent polymer are disclosed. The devices include molecularly oriented polymers comprising recurring units (L) which exhibit a distribution of high electron density about the long axes (X) of the polymer and the recurring units (L) thereof. Transparent birefringent polymers comprising a plurality of recurring units (L) having a substantially cylindrical distribution of electron density about the long axis (X) of such units and the chain-extended polymers are included in optical devices and articles. The polymers exhibit high birefringence and simulate in a polymer the optical properties of a uniaxial crystal.

FIG 1
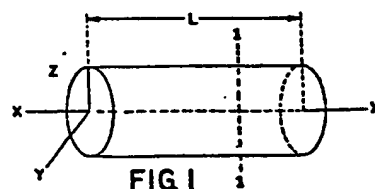
Specification

BACKGROUND OF THE INVENTION

This invention relates to an optical device or article. More particularly, it relates to such an article or device including a molecularly oriented highly birefringent polymeric material.

Materials having a birefringent character have been variously applied in connection with the construction of filter and other optical devices. Frequently, a birefringent element utilized in an optical filter or other device will comprise a plate made from a monocrystalline form of birefringent material. Single crystals are expensive materials and are not readily formed to the desired shape or conformation required in particular applications. The size to which crystals can be grown represents an additional limitation on the utilization of such materials in optical devices.

Optical devices including a birefringent material in the form of a polymeric layer, such as may be formed by the unidirectional stretching of a suitable polymeric material, have also been described. Thus, light-polarizing devices utilizing a polymeric birefringent layer have been described in U.S. Patent 3,213,753 (issued October 26, 1965 to H.G. Rogers). Optical devices including polymeric birefringent materials have also been set forth, for example, in U.S. patent 3,506,333 (issued April 14, 1970 to E.H. Land) and in U.S. Patent 3,610,729 (issued October 15, 1971 to H.G. Rogers). Frequently, the efficiency of an optical filter, polarizing or other optical device including a birefringent element or layer will depend upon the realization of large net differences in refractive index between a birefringent material and adjacent or contiguous layers. In general, such net differences will be maximized where a birefringent material is highly birefringent. Correspondingly, large net differences in refaction indices of contiguous layers will be unattainable

1 where birefringent polymeric materials otherwise suited to
application in an optical device tend to exhibit either low
or only marginal birefringent character. Accordingly,
optical devices including polymeric layers or elements ex-
hibiting a highly birefringent character will be of

5 particular interest for optical applications and enhanced
efficiency.

SUMMARY OF THE INVENTION

10 The present invention provides an optical device or article
which includes a molecularly oriented and optically uni-
axial highly birefringent polymer. The polymer comprises
repeating molecular units exhibiting high electron density
substantially cylindrically distributed about the long axis

15 of the polymer and the repeating units thereof. It has been
found that the birefringent character of a polymer is
importantly releated to the molecular configuration or
structure of the repeating units of the polymer and to the
distribution of electron density about the long axis of the

20 polymer and the repeating units thereof. Thus, it has been
found that the provision, in a transparent polymeric
material comprising a plurality of repeating units in
chain-extended relationship, of a substantially cylindrical
distribution of electron density about the long axis of the

25 polymer permits the realization of high birefringence and
the simulation in a polymeric material of optical
properties of a uniaxial crystal.

The present invention, thus, provides an optical device or

30 article including a transparent molecularly oriented highly
birefringent polymer, said highly birefringent polymer
comprising repeating molecular units exhibiting high
electron density substantially cylindrically distributed
about the long axes of the polymer and the repeating units

35 thereof, said highly birefringent polymer being optically

1 uniaxial exhibiting only two indices of refraction. It has
been found that birefringence of a polymeric material useful
in articles or devices of the present invention exhibit bi-
refingence in relation to the molecular configuration of the
·repeating molecular units and the cylindrical or ellipsoidal
5 electron density distribution about the axes of the polymer
and the recurring units thereof, said birefringence being
in relation to said molecular configuration and said
electron ·density distribution according to a dimensionless
geometric index G represented by the relationship
10

$$G = 0.222 \times E \times \frac{L}{D}$$

where in E is a dimensionless eccentricity factor defined
by the relationship
15

$$E = \frac{1 + e_L}{1 + e_T}$$

where e_L is the longitudinal eccentricity of the polarizab-
20 ility of the repeating molecular unit and e_T is the trans-
verse eccentricity of the electron polarizability of the
repeating molecular unit, L is the length of the repeating
molecular unit along the main axis thereof and D is the mean
diameter of the repeating molecular unit.
25
A preferred article of the present invention is a multi-
layer light-transmitting device including at least one
additional transparent layer having an index of refraction
substantially matching one index of refraction of said
30 layer of transparent molecularly oriented highly bire-
fringent polymeric material and comprising isotropic or
birefringent material; said at least one additional trans-
parent layer, when a layer of birefringent material, having
one index of refraction thereof substantially different from
35 one index of refraction of said layer of transparent mole-

1 cularly oriented highly birefringent polymeric material and
having a molecular orientation substantially perpendicular
to the molecular orientation of said molecularly oriented
hightly birefringent polymeric material.

5   THE DRAWINGS

      Fig. 1   is a geometric representation of molecular di-
                  mensions of a repeat unit of a polymeric material.

10 Fig. 2   is a cross-sectional view along the line 1-1 of
                  Fig. 1.

      Fig. 3   is a vectorial representation of bond and group
                  polarizabilities of a repeat unit of a polymeric
15   material.

      Figs. 4a and 4b show, respectively, ellipsoidal and circular
                  cross-sectional distribution of electron density
                  about the long axis of a recurring unit of a
20   polymeric material.

      Fig. 5   is a diagrammatic fragmentary edge view of a
                  light-transmitting device of the present invention
                  illustrating the transmission of light rays
25   therethrough.

      Fig. 6   is a diagrammatic side view of an automotive
                  vehicle headlamp which includes a light-polarizing
                  filter of the invention.

30
      Fig. 7   is a diagrammatic fragmentary edge view of another
                  embodiment of the present invention showing in-
                  cident light thereon being partly transmitted and
                  partly reflected as separate linearly polarized
35   components vibratiing in orthogonal directions.

1 Fig. 8   is a diagrammatic side view of an optical beam-
             splitter device including a birefringent poly-
             meric material.

DETAILED DESCRIPTION OF THE INVENTION

5

As indicated hereinbefore, the present invention provides
an optical device including a transparent, molecularly
oriented and highly birefringent polymeric material. The
birefringent polymeric material of the devices of the in-
10   vention comprises repeat molecular units which exhibit
high electron density substantially cylindrcally distributed
about the long axes of the polymer and the repeat units
thereof. The polymeric material, comprised of repeating
units of molecular structure such as to provide a sub-
15   stantially cylindrical distribution of electron density
about the long axis or backbone of the polymer, exhibits
optical anisotropy or birefringence in accordance with the
relationship

20
$$G = 0.222 \left(\frac{1 + e_L}{1 + e_T} \right) \frac{L}{D}$$

where G represents the geometric index of a repeating unit;
e_L is the longitudinal eccentricity of the electron polar-
25   izability of the repeating molecular unit; e_T is the trans-
verse eccentricity; L is the length of the repeating unit
along the main axis thereof; and D is the mean diameter of
the repeating molecular unit. The contribution to bire-
fringence of the molecular structure of a repeating, chain-
30   extending unit and of electron density distribution will
be better understood by reference ot the drawings hereof.

In Fig. 1 is shown a geometrical representation of a
repeating chain-extending molecular unit of a polymeric
35   material. Each repeating unit may thus be visualized as a

1   repeating rod-like segment of finite length L and of a
generally cylindrical configuration. Birefringence has been
found to be importantly related to the molecular structure
of the repeating units of the polymer in accordance with
the relationship of geometric index G, set forth herein-
5   before. A highly birefringent polymeric material useful in
the optical devices hereof will thus comprise a plurality
of molecular units in chain-extended relationship, each
unit having a length L, shown in Fig. 1. The long axis X of
each repeating unit forms, in the chain-extended polymer,
10   the long axis or backbone. Each axis in Fig. 1 forms a
right angle with respect to any other axis. The mean dia-
meter D, set forth in the geometric index G, is determined
for each repeating unit by the expression

15    $D = \frac{Y + Z}{2}$. In Fig. 2 is shown along line 1-1 of Fig. 1, a
cross-sectional view. The shown Y and Z axes are at right
angles to one another, the X axis comprising the axis of
the cylinder extending in a direction normal to the plane
of the paper.
20

In addition to a rigid rod-like geometry in a polymeric
material as the result of an end-to-end combination of
repeating units, the electron density distributed around
the long axis of the polymer, variously treated as a
25   cylindrical or ellipsoidal distribution, is believed to
comprise a major contributing factor to optical anisotropy
or birefringence. High electron density substantially
cylindrically distributed around the long axis of a polymer
is exhibited, for example, in a polymer of coaxially-bonded
30   repeating units comprising non-coplanar, particularly
orthogonal, biphenyl groups. An orthogonal relationship
between adjacent phenylene rings can be nearly attained by
the placement of substituents with large steric effects on
at least one ortho-position of each ring, relative to the
35   inter-ring bond. In Fig. 3 is shown a vectorial represent-
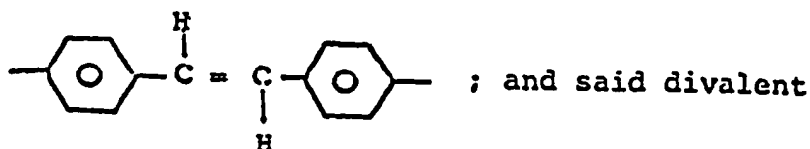
$$-\underset{}{\bigcirc} - \overset{H}{\underset{H}{C}} = \overset{}{\underset{}{C}} - \bigcirc - \quad \text{; and said divalent}$$

radical B is a substituted quaterphenylene radical having the formula

$$-\bigcirc - \bigcirc - \bigcirc - \bigcirc -$$
$$W_p \quad X_r \quad X_r \quad W_p$$
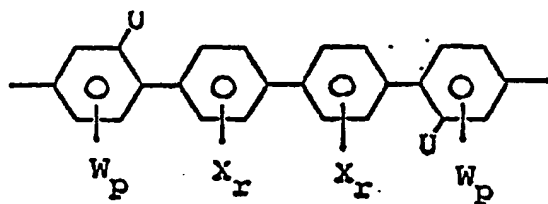
wherein each U is a substituent other than hydrogen, each W is hydrogen or a substituent other than hydrogen, each p is an integer from 1 to 3, each X is hydrogen or a substituent other than hydrogen and each r is an integer from 1 to 4, said U, W_p and X_r substitution being sufficient to provide said radical with a non-coplanar molecular configuration.

24. A device according to claims 22 or 23 each of U and X_1 in said formula of radical B is a substituent selected from the group consisting of halogen, nitro, alkoxy and trifluoromethyl.

25. A multilayer light-transmitting device comprising, in assembled bonded relation: a layer of transparent molecularly oriented highly birefringent polymer according to any of the preceding claims; said multilayer light-transmitting device including at least one additional transparent layer having an index of refraction substantially matching one index of refraction of said layer of transparent molecularly oriented highly birefringent polymeric material and comprising isotropic or birefringent material; said at least one additional transparent layer, when a layer of birefringent material, having one index of refraction

1   thereof substantially different from one index of refract-
ion of said layer of transparent molecularly oriented
highly birefringent polymer and having a molecular orient-
ation substantially perpendicular to the molecular orient-
ation of said molecularly oriented highly birefringent

5   polymer.

26. A multilayer light-transmitting device according to
claim 25 wherein said layer of transparent molecularly
oriented highly birefringent polymer is bonded to a trans-

10   parent layer having an index of refraction substantially
matching one index of refraction of said transparent
molecularly oriented highly birefringent polymer.

27. A multilayer light-transmitting device according to
15   claim 25 wherein said layer of transparent molecularly
oriented highly birefringent polymer is bonded between two
transparent layers, one transparent layer having in index
of refraction substantially matching the lower index of
refraction of said transparent molecularly oriented highly

20   birefringent polymer.

28. A multilayer light-transmitting device according to
claim 27 wherein one of said two transparent layers has an
index of refraction substantially matching the lower index

25   of refraction of said transparent molecularly oriented
highly birefringent polymeric material and the second of
said two transparent layers has an index of refraction
substantially matching the higher index of refraction of
said transparent molecularly oriented highly birefringent

30   polymer.

29. A multilayer light-transmitting device according to
claim 25 comprising an alternating arrangement of a
plurality of layers of said molecularly oriented highly

35   birefringent polymer and a plurality of said additional

1 index value of 1.2 or higher. Experimentally determined
birefringence values for polymeric materials have been found
to correlate with calculated geometric indices. For example,
a geometric index of 1.20 was calculated for the recurring
structural unit of the following polymer:

5
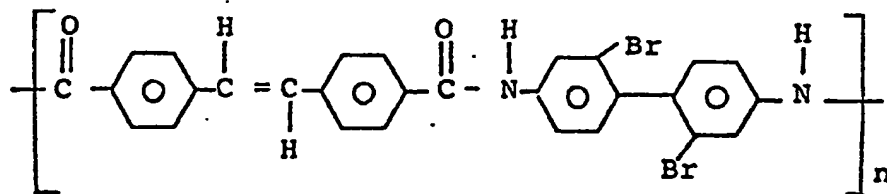
10

Theoretical maximum birefringence (Δn_{max}) was obtained by
plotting the orientation function for the polymer (calculated
from infrared dichroism) against the measured birefringence
15 of the polymer and extrapolating to 100 % orientation. A
Δn_{max} value of 1.20 was obtained. In like manner, a
correlation of geometric index G of 1.18 and Δn_{max} of 0.98
was obtained in connection with the following polymer
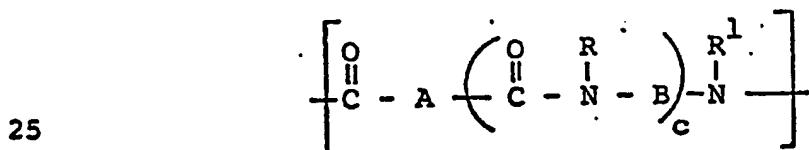comprising the shown recurring unit:

20
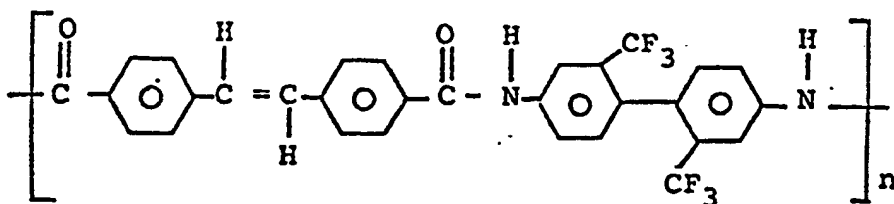
25

A number of polymeric materials comprising recurring units
having a geometric index as hereinbefore defined of about
0.5 or higher can be suitably employed in oriented form as
a birefringent polymeric material in an optical device of
30 the present invention. Rigid rod-like polymeric materials
comprised of recurring or repeating divalent units having
interbonded p-phenylene moieties of non-coplanar molecular
configuration are especially suited herein and are generally
characterized by geometric index values of one or greater
35 and by high birefringence. Exemplary of recurring units of

1   high geometric index G and high birefringence are certain
polyamide materials including recurring units comprised,
for example, of interbonded aromatic rings where the
aromatic rings are in twisted relation to one another, i.e.,
where the aromatic rings are in a non-coplanar molecular
5   configuration with respect to each other or, preferably, in
mutually orthogonal planes. It has been found that the
presence of substituent moieties on interbonded aromatic
radicals, of type and position such as to effect a non-
coplanar molecular configuration with respect to the inter-
10   bonded aromatic radicals, provides a recurring unit having
a high . geometric index. The condition of non-coplanarity
among aromatic rings in a recurring unit, or presence in
such units of rings in "twisted" configuration relative to
one another has been found to be importantly related to
15   high birefringence in the rigid rod-like oriented polymers
resulting from the end-to-end joining of such recurring
units.

Among polyamide materials suited to application as highly
20   birefringent layers in the devices of the invention are
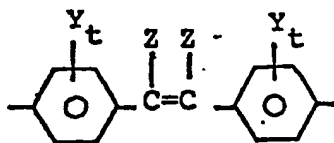polyamides comprising repeating units of the formula .

$$\left[\begin{array}{c} O \\ \parallel \\ C \end{array} - A \left(\begin{array}{ccc} O & R \\ \parallel & \mid \\ C - N - B \end{array} \right)_c \begin{array}{c} R^1 \\ \mid \\ N \end{array} \right]$$

25

wherein each of A and B is a divalent radical, except that
B can additionally represent a single bond; R and R^1 are
30   each hydrogen, alkyl (e.g., methyl, ethyl), aryl (e.g.,
phenyl, naphthyl), alkaryl (e.g., tolyl), aralkyl (e.g.,
benzyl); c is zero or one; and wherein, when c is one, at
least one of A and B is a divalent radical selected from
the group consisting of:

35

(1) a divalent substituted biphenyl radical
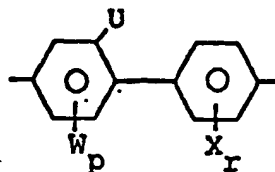
$$\text{structure: biphenyl with substituent U at top, } W_p \text{ below, } X_r \text{ on second ring}$$

where U is a substituent other than hydrogen, each W
is hydrogen or a substituent other than hydrogen, p is
an integer from 1 to 3, each X is hydrogen or a sub-
stituent other than hydrogen and r is an integer from
1 to 4, said U, Wp and Xr substitution being sufficient
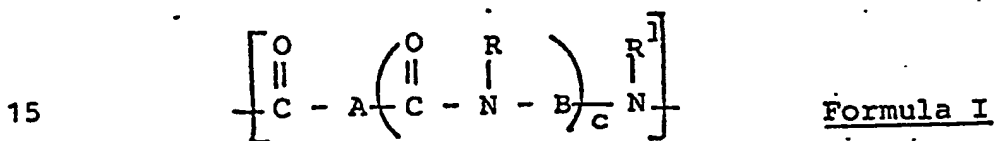to provide said radical with a non-coplanar molecular
configuration; and

(2) a divalent substituted stilbene radical

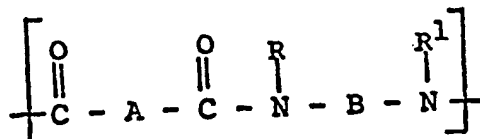$$\text{structure: } Y_t \text{ substituted phenyl} - C=C \text{ (each bearing Z)} - Y_t \text{ substituted phenyl}$$

where each of Y and Z is hydrogen or a substituent
other than hydrogen and each t is an integer from
1 to 4, with the proviso that when each said Z is
hydrogen, at least one said Y substituent is a sub-
stituent other than hydrogen positioned on the
corresponding nucleus ortho with respect to the

$$-\overset{\text{Z}}{\underset{|}{\text{C}}}= \text{ moiety of said radical, said Z and } Y_t \text{ substitution}$$

being sufficient to provide said radical with a non-
coplanar molecular configuration;

and wherein, when c is zero, A is a divalent radical
selected from the group consisting of radicals (1) and (2)
as hereinbefore defined.

As used herein, substitution sufficient to provide a
radical with a non-coplanar molecular configuration refers
to substitution of type and position effective to confer
to the interbonded aromatic radical thereof a non-coplanar
molecular configuration such that the value of the geo-
metric index, as hereinbefore defined, is about 0.5 or
higher. Preferably, the nature of such substitution will be
sufficient to provide a G value of 1.0 or higher, and most
preferably, 1.2 or higher.

As described hereinbefore, birefringent polyamides useful in
devices of the present invention include those comprising
recurring units of the formula

$$\left[\begin{matrix} O \\ \| \\ C \end{matrix} - A \left(\begin{matrix} O \\ \| \\ C \end{matrix} - \begin{matrix} R \\ | \\ N \end{matrix} - B\right)_c \begin{matrix} R^1 \\ | \\ N \end{matrix}\right] \qquad \underline{Formula\ I}$$

wherein c is zero or one and wherein A (when c is zero) or
at least one of A and B (when c is one) comprises a sub-
stituted divalent biphenyl radical or a sub-
stituted divalent stilbene radical. Thus, when c is zero,
divalent radical A comprises a substituted biphenylene
radical having a non-coplanar molecular configuration or a
substituted divalent stilbene radical of non-coplanar molec-
ular configuration. Similarly, when c is the integer one,
one or both of divalent radicals A and B comprises such sub-
stituted biphenylene or substituted stilbene radicals. It
is preferred from the standpoint of ease of preparation
that each of R and R^1 be hydrogen, although each of R and
R^1 can be alkyl, aryl, alkaryl or aralkyl.

From inspection of the general formula set forth as
descriptive of recurring units of the polyamides of
Formula I, it will be appreciated that polyamides comprising
the following recurring units are contemplated when c is one:

1

$$\left[\begin{array}{ccccccc} O \\ \parallel \\ C \end{array} - A - \begin{array}{c} O \\ \parallel \\ C \end{array} - \begin{array}{c} R \\ \mid \\ N \end{array} - B - \begin{array}{c} R^1 \\ \mid \\ N \end{array} \right]$$ Formula II

5 In such recurring units, at least one of divalent radicals
A and B will comprise a substituted biphenylene or sub-
stituted stilbene radical of non-coplanar, molecular con-
figuration conforming to the formulae

10
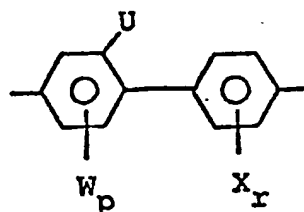
; Formula III

15   or
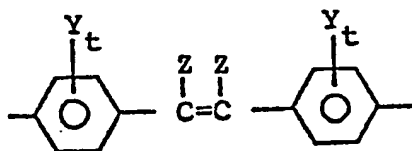
. Formula IV

20
Where only one of said A and B radicals is a substituted
biphenylene or substituted stilbene radical conforming to
the radicals represented by the structures of Formulas III
and IV, the remaining A or B radical can comprise any of a
25 variety of divalent radicals so long as the birefringent
properties of the polyamide material are not effectively
negated. In general, where only one of the A and B radicals
conforms to the structures represented by Formulas III
and IV, the remaining A or B radical will desirably be a
30 divalent radical which does not confer transverse
eccentricity to the recurring unit. Similarly, where one
of radicals A or B is a radical which confers transverse
eccentricity to the recurring unit, the other of radical A
or B will desirably be a radical which confers high long-
35 itudinal eccentricity such that the recurring unit of the

1 polymer exhibits a high geometric index. Suitable divalent radicals include, for example, unsubstituted biphenylene or stilbene radicals; phenylene; trans-vinylene; or ethynylene. Also suitable are polyunsaturated divalent radicals conforming to the formula

5

$$:\left(\begin{array}{c} \overset{E}{\underset{D}{\overset{|}{C}}} = \overset{|}{\underset{}{C}} \end{array}\right)_n$$
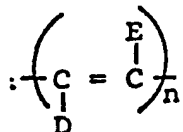
10 where n is an integer of at least two (e.g., two or three) and each of D and E is hydrogen or alkyl (e.g., methyl) and inclusive of such polyunsaturated divalent radicals as

trans-trans-1,4-butadienylene, i.e., $-\overset{H}{\underset{H}{\overset{|}{C}}}=\overset{H}{\underset{H}{\overset{|}{C}}}-\overset{}{C}=\overset{}{C}-$; and 1,4-

15

dimethyl-trans-trans-1,3-butadienylene, i.e., $-\overset{CH_3}{\overset{|}{C}} = \overset{H}{\overset{|}{C}} - \overset{H}{\overset{|}{C}} = \overset{}{\underset{CH_3}{\overset{|}{C}}} -$.

It will appreciated that compounds containing amino groups
20 directly attached to carbon atoms having linear unsaturated radicals are not stable and that, accordingly, the afore-said vinylene, ethynylene and butadienylene radicals cannot serve as B radicals in the recurring units repre-sented by the structure of Formula II.

25

In general, from the standpoint of maximized birefringent properties, it will be preferred that each of radicals A and B comprise a divalent radical exhibiting a non-coplanar molecular configuration and conforming to the structures of Formulas III or IV. It will be appreciated, however,
30 that the particular nature of such A and B radicals may affect the ability to readily orient the polyamide material, as by extrusion, stretching or the like. Accordingly, where the ability of a polyamide material to be oriented is
35 effectively reduced by the presence in the polyamide of

1   each of radicals A and B of non-coplanar molecular configur-
ation and conforming to the structures of Formulas III or
IV, it will be preferred that only one of such radicals A
and B of the polyamide material conform to the structure
of Formulas III or IV.

5

In the case of radicals A and/or B of the recurring type
represented by Formula III, U will comprise a substituent
other than hydrogen; W will be either hydrogen or a sub-
stituent other than hydrogen; and p will be an integer of
10   from 1 to 3. In the case of such radicals, X will be
hydrogen or a substituent other than hydrogen and r will be
an integer of from 1 to 4. It will be appreciated from the
nature of U, W, p, X and r, as set forth, that at least
one aromatic nucleus of the biphenylene radical represented
15   by Formula III will be substituted by a moiety other than
hydrogen and that such substituent, U, will be positioned
in an ortho relationship to the bridging carbon atoms of
the biphenylene nuclei. Preferably, each aromatic nucleus
of the biphenylene radical of Formula III will contain a
20   substituent other than hydrogen positioned in an ortho
relationship to the bridging carbon atoms of the bi-
phenylene radical of Formula III and in this case, the
divalent radical will have the following formula

25
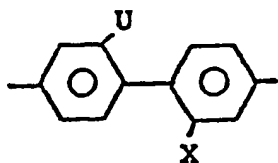
Formula V

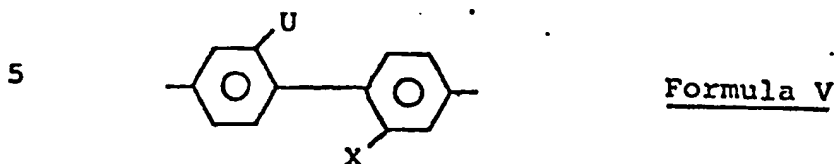30   wherein each of U and X comprises a substituent other than
hydrogen.

The nature and positioning of substituents U, W and X of
the biphenylene radical of Formula III can vary widely,
35   consistent with the provision of a biphenylene radical

1 having a non-coplanar molecular configuration. While
applicants do not wish to be bound by precise theory or
mechanism in explanation of the highly birefringent
character observed in oriented polymers comprising recurring
units of high geometric index, it is believed that the non-
5 coplanar character conferred or promoted by the presence in
a polymer of such recurring units provides a distribution
of high electron density cylindrically about the long axis
of the polymer. This distribution is believed to be
importantly related to unusually high birefringence .
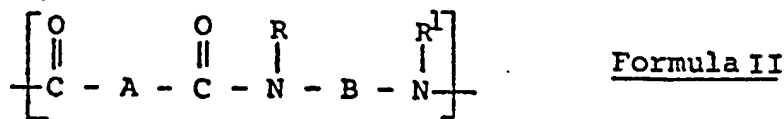10 observed in such polymers.

The nature of substituency, U, Wp and Xr should be such as
to provide the biphenylene radical of formula III with a
non-coplanar molecular configuration referred to herein-
15 before. Such configuration will in part be determined by
the positioning and size of non-hydrogen substituents on the
aromatic nuclei of the biphenylene radical and upon the
number of such substituents on such aromatic nuclei. For
example, where the biphenylene radical contains a single
20 non-hydrogen substituent, i.e., substituent U, the nature
and, in particular the size of such U substituent, should
be such as to provide the desired non-coplanar molecular
configuration. Suitable U substituents herein include
halogen (e.g., fluoro, chloro, bromo, iodo); nitro; alkyl
25 (e.g., methyl, ethyl); alkoxy (e.g., methoxy); substituted-
alkyl (e.g., trifluoromethyl or hydroxymethyl); cyano;
hydroxy; thioalkyl (e.g., thiomethyl); carboxy; sulfonic
acid esters; sulfinic acid esters; carboxyamide; sulfon-
amide; amino; and carbonyl. Substituent X can comprise
30 hydrogen or any of the substituents set forth in connection
with substituent U. Preferably, at least one X substituent
will comprise a substituent other than hydrogen. Each
substituent W can comprise hydrogen or a substituent other
than hydrogen as set forth in connection with substituents
35 U and X. Normally, W will be hydrogen and p will be the
integer 3.

1 Preferred polyamides herein are the polyamides comprising
recurring units having the biphenylene radical of
Formula V, i.e.,

5

Formula V

wherein each of U and X is a substituent other than
10 hydrogen. The presence of such non-hydrogen substituents
on each of the aromatic nuclei of the radical promotes a
condition of non-coplanarity. Examples of such preferred
substituents, which may be the same or different, include
halo, nitro, alkoxy and substituted-alkyl (e.g., trifluoro-
15 methyl). While the presence of such non-hydrogen sub-
stituents is preferred from the standpoint of promoting
non-coplanarity, it will be appreciated from the nature of
substituents W and X set forth in connection with Formula III
hereinbefore, that each X and W can be hydrogen and that,
20 accordingly, substituent U will in such instance desirably
comprise a bulky substituent such as will provide steric
hindrance to a condition of coplanarity.

In the polyamides of the present invention which comprise
25 recurring units represented by the following formula

$$\left[\begin{array}{c} O \\ \parallel \\ C \end{array} - A - \begin{array}{c} O \\ \parallel \\ C \end{array} - \begin{array}{c} R \\ \mid \\ N \end{array} - B - \begin{array}{c} R^1 \\ \mid \\ N \end{array} \right]$$ Formula II

30 either or both of radicals A and B can comprise the sub-
stituted stilbene radical set forth hereinbefore as
Formula IV, i.e.,

35

Formula IV
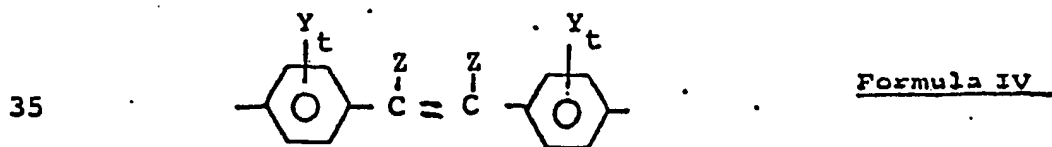
1 In such stilbene radicals, the nature of each Y and Z will
be such as to provide the radical with a non-coplanar
molecular configuration. Preferably, non-coplanarity will
be provided by the presence of a single non-hydrogen sub-
stituent Z. Where each Z is hydrogen, non-coplanarity can

5 be provided by the positioning of a non-hydrogen Y sub-
stituent on at least one aromatic nucleus of the radical in

an ortho relationship to the $-\overset{\overset{Z}{|}}{C}=$ moiety of the radical.
Suitable non-hydrogen Y and Z substituents include, for

10 example, any of those set forth in connection with radicals
U, W and X defined hereinbefore.

Examples of preferred stilbene-type radicals included
within the class represented by Formula IV include the

15 following:
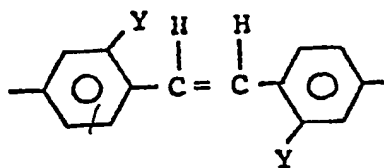
Formula VI

20

where at least one of the Y substituents is other than
hydrogen, preferably, halo or alkoxy; and
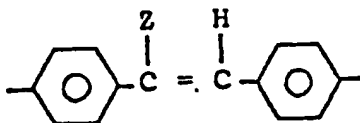
Formula VII

25

where Z is a substituent other than hydrogen, preferably
halo.

30

Inclusive of polyamides of the present invention represented
by the structure of Formula II are those having recurring
units represented by the following structures wherein,
unless otherwise specified, U, W, p, X, r, Y and t have

35 the meanings set forth hereinbefore:

1

$\left[\begin{array}{c} \underset{C}{\overset{O}{\parallel}} \end{array} \right.$ ... U ... W$_p$ ... X$_r$ ... $\overset{O}{\overset{\parallel}{C}}$ — N — ... U ... W$_p$ ... X$_r$ ... N $\left. \vphantom{} \right]$;   <u>Formula VIII</u>
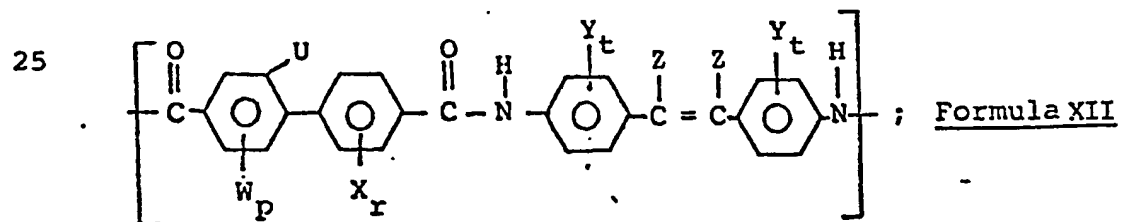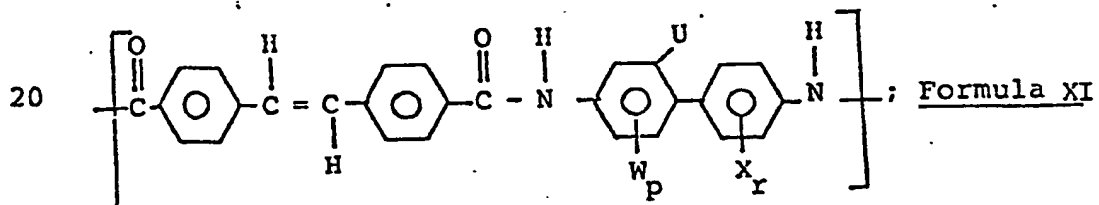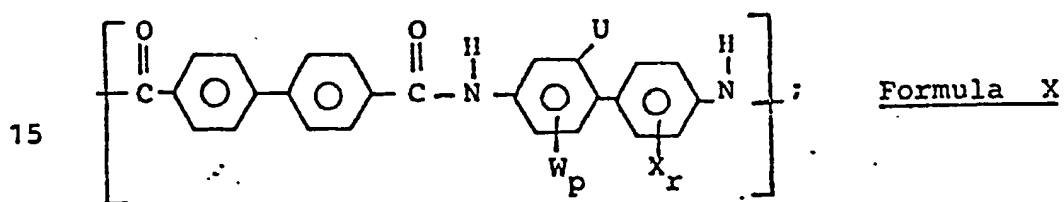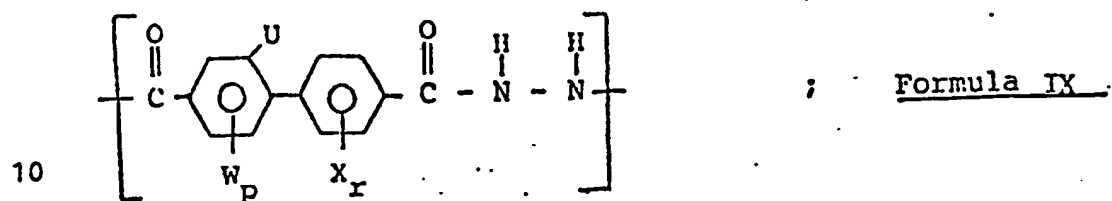
5

$\left[\begin{array}{c} \underset{C}{\overset{O}{\parallel}} \end{array} \right.$ ... U ... W$_p$ ... X$_r$ ... $\overset{O}{\overset{\parallel}{C}}$ — N — N $\left. \vphantom{} \right]$;   <u>Formula IX</u>

10

$\left[\begin{array}{c} \underset{C}{\overset{O}{\parallel}} \end{array} \right.$ ... $\overset{O}{\overset{\parallel}{C}}$ — N — ... U ... W$_p$ ... X$_r$ ... N $\left. \vphantom{} \right]$;   <u>Formula X</u>

15

20

$\left[\begin{array}{c} \underset{C}{\overset{O}{\parallel}} \end{array} \right.$ ... $\overset{H}{\underset{H}{C}}$ = C ... $\overset{O}{\overset{\parallel}{C}}$ — N — ... U ... W$_p$ ... X$_r$ ... N $\left. \vphantom{} \right]$; <u>Formula XI</u>

25

$\left[\begin{array}{c} \underset{C}{\overset{O}{\parallel}} \end{array} \right.$ ... U ... W$_p$ ... X$_r$ ... $\overset{O}{\overset{\parallel}{C}}$ — N — ... Y$_t$ ... C = C ... Y$_t$ ... N $\left. \vphantom{} \right]$; <u>Formula XII</u>

30

35
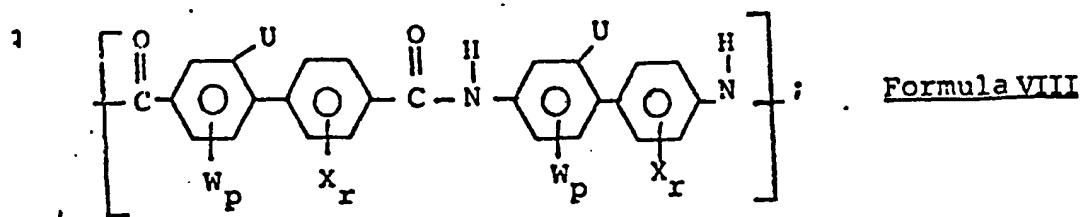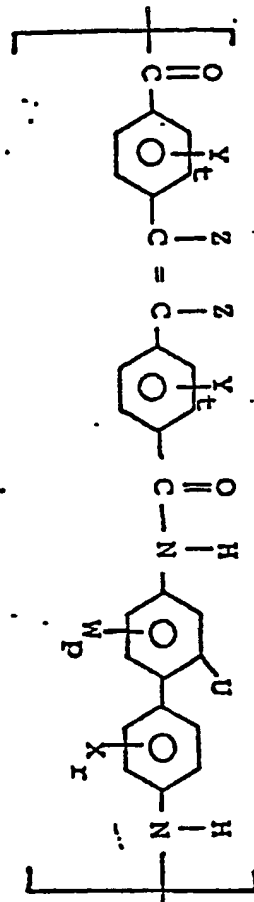
Formula XV.

Formula XIV
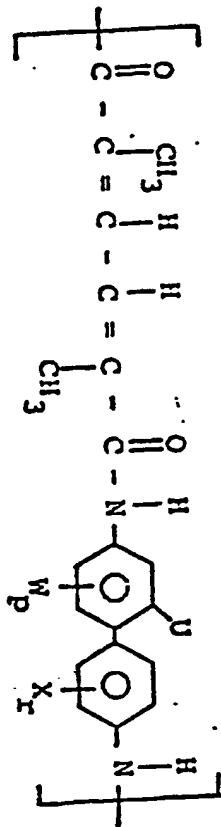
Formula XIII
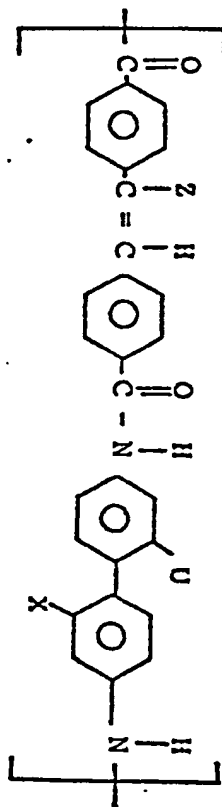
where each X is other than hydrogen.
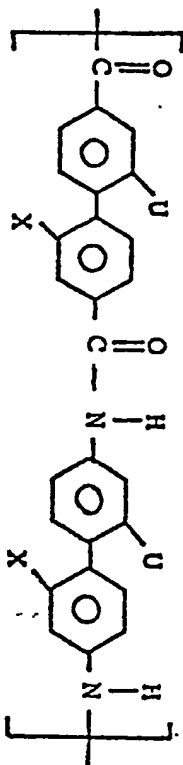
where Z and X are other than hydrogen; and

Formula XVII

Formula XVI

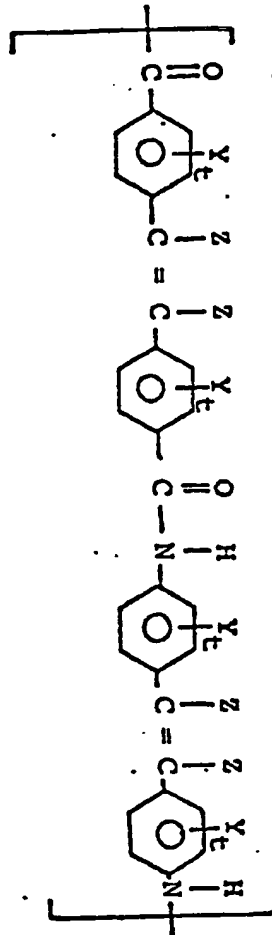From inspection of the general formula set forth as descriptive of recurring units of the polyamides, i.e. recurring units of the formula
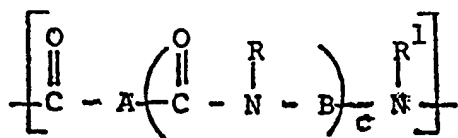
$$\left[\overset{O}{\underset{\parallel}{C}} - A \left(\overset{O}{\underset{\parallel}{C}} - \overset{R}{\underset{\mid}{N}} - B \right)_c \overset{R^1}{\underset{\mid}{N}} \right]$$
,   Formula I

1   it will be appreciated that, when c is zero, the recurring
units will be represented by the following formula:
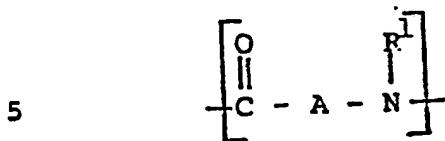
$$\left[\begin{array}{c} O \\ \parallel \\ C - A - N \end{array} \begin{array}{c} R^1 \\ \mid \\ \end{array}\right]$$ Formula XVIII

In such recurring units, radical A will comprise a divalent
radical having a non-coplanar molecular configuration and
10 conforming to the structures of Formulas III and IV set
forth hereinbefore, i.e.,
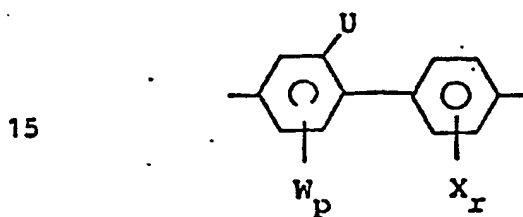
Formula III

or
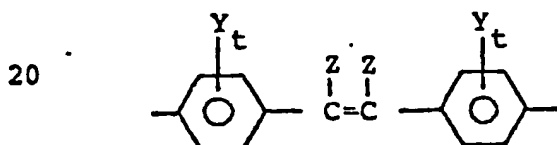
Formula IV

where U, W, p, X, r, Y, t and Z have the same meanings.

25

Inclusive of polyamides represented by the structure of
Formula XVIII are those having recurring units represented
by the following structures wherein U, W, p, X, r, Y
and t, unless otherwise indicated, have the meanings set
30 forth hereinbefore:

35

1

; <u>Formula XIX</u>

5
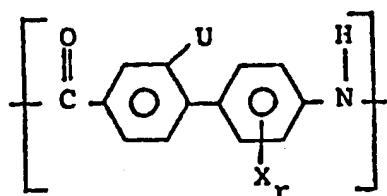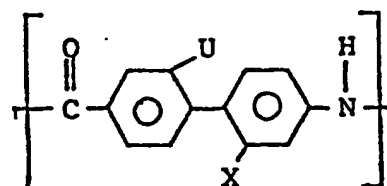
; <u>Formula XX</u>

10 where X is other than hydrogen;

; <u>Formula XXI</u>

15

, <u>Formula XXII</u>

20
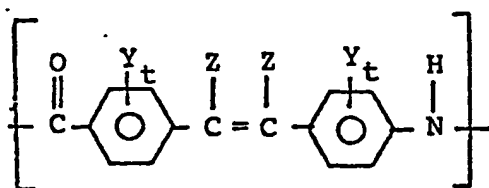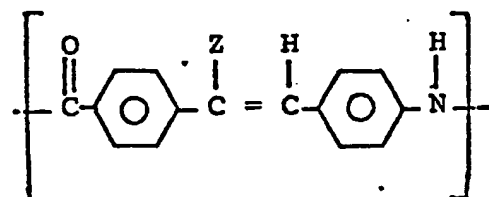
where Z is other than hydrogen.

25 While the polyamides described herein consist essentially
of recurring units represented by the structures of
Formulas II and XVIII, i.e., recurring units of the
formulas

30

a combination of such recurring units, the polyamides can

35

1   also comprise recurring units not conforming to the
described structures of Formulas II and XVIII. Examples
of recurring units which do not conform to such descriptions
and which can be present in such polyamides in proportions
which do not negate the high birefringence of the poly-

5   meric material include, for example, recurring units having
the formulas

$$-\overset{\overset{O}{\|}}{C} - G - \overset{\overset{O}{\|}}{C}- \quad , \qquad \text{Formula XXIII}$$

10

$$-\overset{\overset{R}{|}}{N} - G - \overset{\overset{R^1}{|}}{N}- \quad , \quad \text{or} \qquad \text{Formula XXIV}$$

$$-\overset{\overset{O}{\|}}{C} - G - \overset{\overset{R}{|}}{N}- \qquad \text{Formula XXV}$$

15
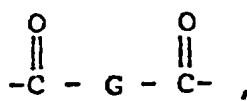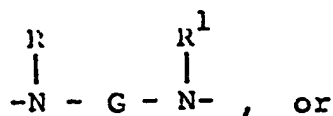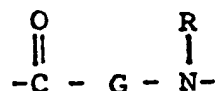
wherein G is a divalent radical such as 1,4-phenylene;
4,4'-biphenylene; vinylene; trans,trans-1,4-butadienylene;
4,4'-stilbene; ethynylene; 1,5-naphthalene; 1,4-dimethyl-

20   trans,trans-1,4-butadienylene; 2,4'-trans-vinylenephenylene;
trans,trans-4,4'-bicyclohexylene; 2,5,7-bicyclooctatriene-
1,4-,

25

i.e., ; or

30
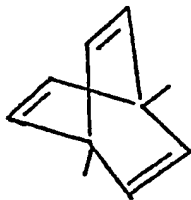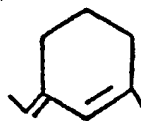
Other divalent radicals can, however, serve as radical G
provided that such radicals do not adversely and materially
reduce the birefringence of the polyamide material. It will
be appreciated that G cannot represent an aliphatic un-

35   saturated moiety where a carbon atom thereof having such
unsaturation is to be bonded to an amino group.

1 The substituted polyamides utilized in devices of the
present invention can be prepared by resort to polyamide
synthesis routes involving the polymerization of suitable
acid halide and amine monomers in an organic solvent which
may contain a solubilizing agent such as lithium chloride
5 or chain-terminating agent where desired. Polyamides of
the type represented by the structure of Formula I can be
prepared, for example, by the reaction of a dicarboxylic acid halide

$$O \quad O$$
$$\| \quad \|$$
of the formula Hal-C-A-C-Hal with a diamine of the formula

$$R \quad R^1$$
10
$$| \quad |$$
H-N-B-N-H, where Hal represents halogen, such as chloro or
bromo and A and B have the meanings hereinbefore set forth,
except that B cannot represent an aliphatic unsaturated
moiety. The reaction can be conducted in an organic solvent
15 such as N-methyl pyrrolidone (NMP), tetramethylurea (TMU)
or a mixture thereof, and preferably, in the presence of
a salt such as lithium chloride to assist in the solubiliz-
ation of reactant monomers and maintenance of a fluid
reaction mixture. The preparation of a polyamide of the
20 present invention can be illustrated by reference to the
preparation of poly(2,2'-dibromo-4,4'-biphenylene)-trans-
α-bromo-p,p'stilbene dicarboxamide, a preferred polyamide
herein, in accordance with the following reaction scheme:

25

30

35

1

5

10

15

20

25

$$Cl-\overset{O}{\underset{\|}{C}}-\!\!\bigcirc\!\!-\overset{Br}{\underset{H}{C}}\!\!=\!\!C-\!\!\bigcirc\!\!-\overset{O}{\underset{\|}{C}}-Cl \;+\; H_2N-\!\!\bigcirc\!\!\overset{Br}{\underset{Br}{}}\!\!\bigcirc\!\!-NH_2$$

$$\xrightarrow[\text{LiCl}]{\text{NMP/THF}}$$

$$\left[-\overset{O}{\underset{\|}{C}}-\!\!\bigcirc\!\!-\overset{Br}{\underset{H}{C}}\!\!=\!\!C-\!\!\bigcirc\!\!-\overset{O}{\underset{\|}{C}}-\overset{H}{\underset{}{N}}-\!\!\bigcirc\!\!\overset{Br}{\underset{Br}{}}\!\!\bigcirc\!\!-\overset{H}{\underset{}{N}}-\right]_n$$
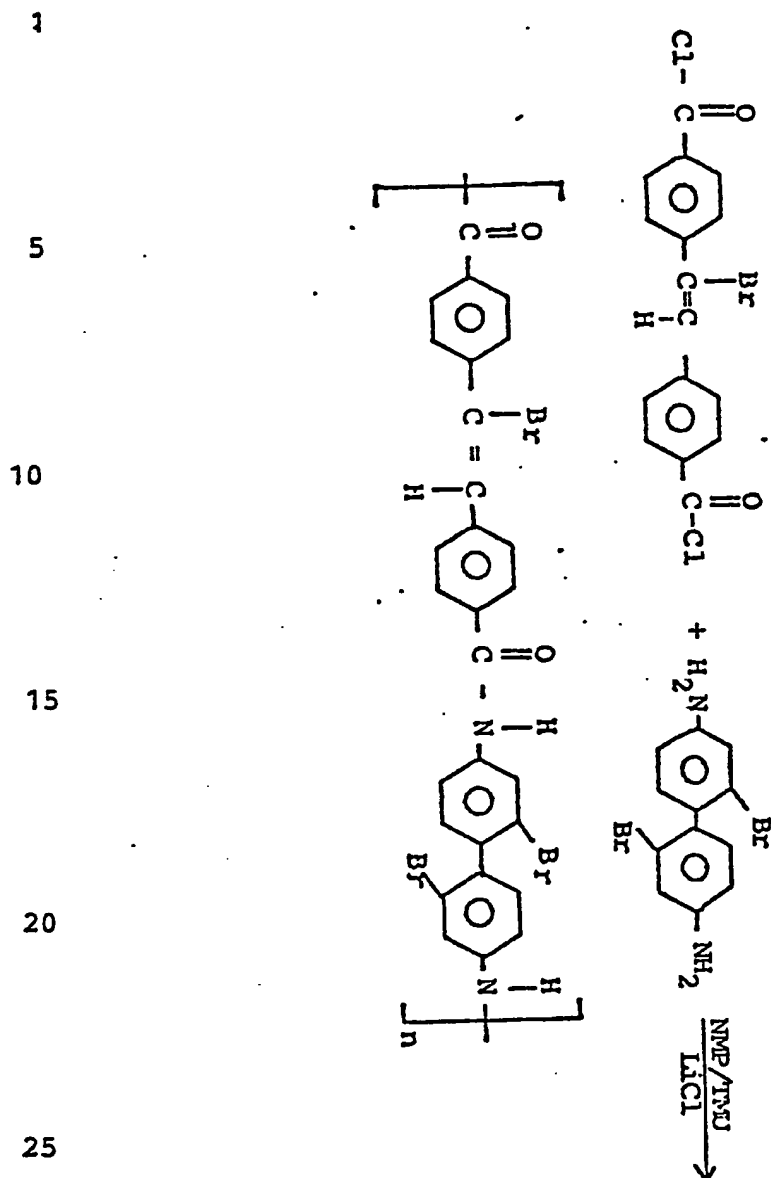
Polyamides containting recurring units having the structure

30

represented by Formula XIII, i.e., $\left[\begin{matrix} O \\ \| \\ C \end{matrix} - A - \begin{matrix} R^1 \\ | \\ N \end{matrix}\right]$
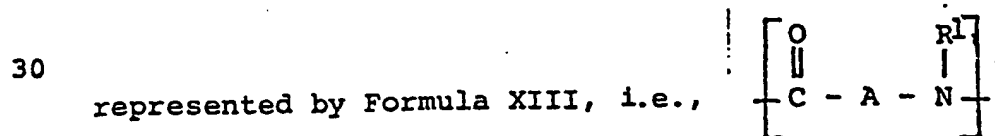
can be prepared, for example, by the polymerization of a
p-amino-aroyl halide monomer in the form of a halide,

35 arylsulfonate, alkylsulfonate, acid sulfonate, sulfate or

1   other salt. This polymerization can be illustrated by
reference to the preparation of poly(2,2'-dibromo-4,4'-
biphenylene)carboxamide in accordance with the following
reaction scheme showing the polymerization of the hydro-
chloride salt of 2,2'-dibromo-4-amino-4'-chlorocarbonyl-
5   biphenyl:
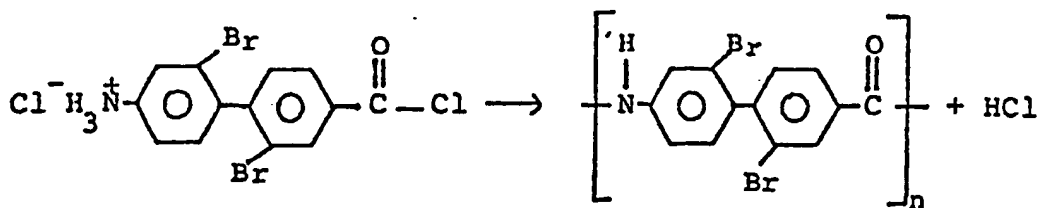
10

Substituted polyamides useful in optical devices of the
present invention can be prepared by polymerization of
15 correspondingly substituted monomers in a suitable organic
reaction solvent. Such solvents include amide and urea
solvents including N-methyl-pyrrolidone and N,N,N'N'-tetra-
methylurea. Other suitable reaction solvent materials
include N-methyl-piperidone-2; N,N-dimethylpropionamide;
20 N-methylcaprolactam; N,N-dimethylacetamide; hexamethyl-
phosphoramide; and N,N'-dimethylethylene urea. The poly-
merization can be conducted by dissolving the monomer or
monomers to be polymerized in the reaction solvent and
allowing the exothermic polymerization reaction to occur
25 usually with the aid of external cooling. In general, the
polymerization will be conducted initially at a temperature
of from about -20°C to about 15°C, and preferably, in the
range of from about -5°C to about 5°C. Thereafter,
usually within about one-half hour to one hour, the
30 reaction will be heated with formation of a thickened poly-
meric mass of gel-like consistency. In general, the poly-
merization reaction will be conducted over a period of from
about 1 to 24 hours, preferably about 3 to 18 hours.

35 While the monomer or monomers to be polymerized can be

1   dissolved in a suitable amide or urea solvent and allowed
   to react with formation of the desired polymeric material,
     a preferred reaction sequence where a mixture of copoly-
     merizable monomers is utilized involves the preparation
     of a solution of a first monomer in the amide or urea
5   solvent and the addition thereto of a second or other
     monomer or a solution thereof in a suitable organic
     solvent therefor, such as tetrahydrofuran. External cooling
     of the resulting reaction mixture provides the desired
     polyamide material in high molecular weight and minimizes
10   the production of undesired side reactions or by-products.

     The polyamide materials prepared as described can be
     recovered by combining the polymerization reaction mixture
     with a non-solvent for the polymer and separating the poly-
15   mer, as by filtration. This can be effectively accomplished
     by blending the polymerization mixture with water and
     filtering the solid polyamide material. The polyamide can
     be washed with an organic solvent such as acetone or ether
     and dried, for example, in a vacuum oven.

20
     Polyamide materials as described hereinbefore and methods
     for their preparation are described in greater detail in
     the European Patent Application of H.G. Rogers, R.A.
     Gaudiana, J.S. Manello and R.A. Sahatjian, Attorney
25   Docket No. 3920-X-11.692 filed of even date herewith.

     While the transparent highly birefringent materials useful
     in the devices of the present invention have been set forth
     by reference to certain polyamides, represented by the
30   structures of Formulas II and XVIII, it will be appreciated
     that transparent highly birefringent polymeric materials
     of other polyamide types, or of types or classes other than
     polyamides, can likewise be utilized herein where the
     repeating units of such polymers have a substantially
35   cylindrical distribution of electron density about the
     long axis of the polymer.

1 Particularly useful herein are transparent polyamide
materials comprising recurring units corresponding to
Formula I hereof wherein c is zero or one, each of A and
B is a divalent radical, except that B can additionally
represent a single bond, and at least one of A and B is
5 a substituted-quaterphenylene radical having the formula
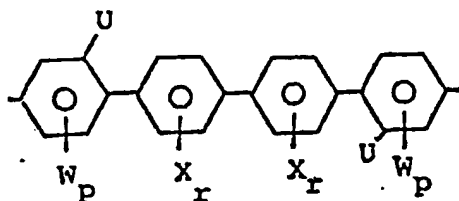
10

wherein U, W, X, p and r have the meanings set forth
herein and the U, W_p and X_r substitution is sufficient to
15 provide the radical with a non-coplanar molecular con-
figuration.

The above substituted-quaterphenylene polyamides can be
prepared, for example, by reaction of a suitably sub-
20 stituted quaterphenylene diamine and a dicarboxylic acid
or halide. These polymers and their preparation are
described in greater detail and are claimed in the
European Patent Application of R.A. Gaudiana and P.S.
Kalyanaraman, (Attorney Docket No. 3920-X-11.692) filed of
25 even date herewith.

Transparent polymeric materials from classes other than
polyamides and which can be utilized herein include, for
example, polymers having thiazole, imidazole, oxazole
30 and/or ester linkages. For example, polymeric materials
comprising the following thiazole-containing recurring
units, where U, W, X, p and r have the meanings herein-
before ascribed, can be utilized herein:

35

1
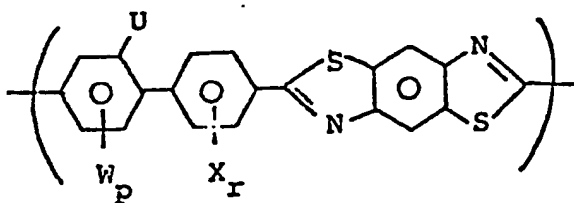
5   Such polymeric materials can be prepared by reaction of a
dicarboxylic acid compound of the formula

10
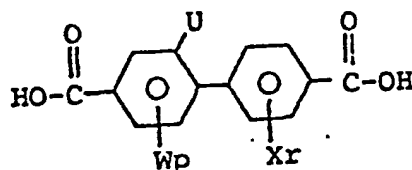
with an amino-thiol of the formula

15
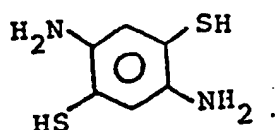
20   in a suitable organic solvent with recovery of the desired
polymeric material.

Polymers comprising the following imidazole-containing
repeating units can also be employed herein, where U, W,
25   X, p and r have the meanings hereinbefore described.

30
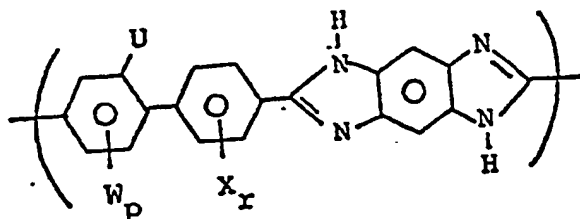
These polymers can be prepared, for example, by reaction
of a dicarboxylid acid compound of the formula

35

1

$$HO-\overset{\overset{\textstyle O}{\|}}{C}-\underset{\underset{\textstyle Wp}{}}{\overset{\overset{\textstyle U}{}}{\bigcirc}}-\underset{\underset{\textstyle Xr}{}}{\bigcirc}-\overset{\overset{\textstyle O}{\|}}{C}-OH$$
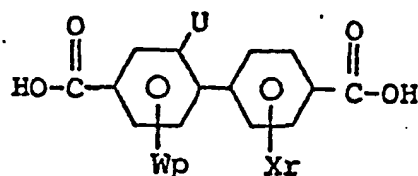
5 with 1,2,4,5-tetramino-benzene.

Polymers containing recurring units having an oxazole
moiety can be suitably prepared by reaction of a dicarb-
oxylic acid compound as aforedescribed with, for example,

10 1,4-dihydroxy-2,5-diamino-benzene, with formation of a
polymer containing the following recurring units where U,
W, X, p and r have the meaning set forth hereinbefore.

15
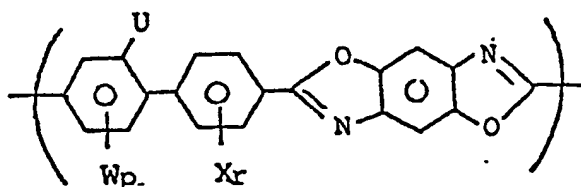
Polyester materials can also be suitably employed herein.

20 Exemplary of such polyesters are those having recurring
units of the formula

25
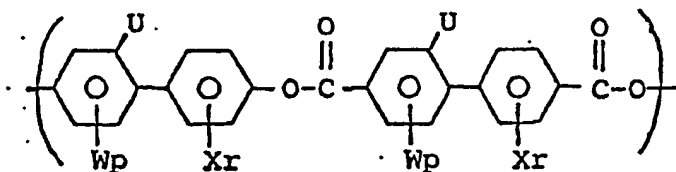
wherein each U, W, X, p and r has the meaning set forth
hereinbefore.

30

Other polymers that can be utilized in optical devices of
the present invention are polymers comprising recurring
units of the formula

35

1

$$-\left[-Mu-\overset{\overset{\displaystyle O}{\|}}{C}-Az-\overset{\overset{\displaystyle O}{\|}}{C}-\right]-$$
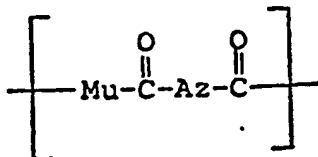
5   where Mu is a divalent radical having the formula

$$-\overset{\overset{\displaystyle D}{|}}{C}=\overset{\overset{\displaystyle E}{|}}{C}-\overset{\underset{\displaystyle D'}{|}}{C}=\overset{\underset{\displaystyle E'}{|}}{C}-$$
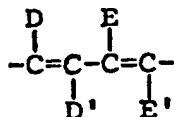
10   where each of D, D', E and E' is hydrogen, alkyl or sub-
stituted-alkyl; and Az is a divalent radical having the
formula

$$-\overset{\overset{\displaystyle R}{|}}{N}-W-\overset{\overset{\displaystyle R'}{|}}{N}-$$

15
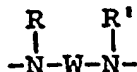
where each of R and R' is hydrogen, alkyl, aryl, alkaryl or
aralkyl and W is a single bond, alkylene or alkenylene; or
Az is a divalent radical having the formula

20

$$-N\overset{\displaystyle Y}{\underset{\displaystyle Y'}{\bigcirc}}N-$$
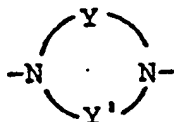
25   where each of Y and Y' represent the atoms necessary to
complete with the nitrogen atoms to which they are bonded
a piperazine or substituted-piperazine radical.

These polymers can be conveniently prepared by reaction of
30   a dienoic acid chloride such as mucononic acid chloride or
α,α'-dimethylmuconic acid chloride with hydrazine or a di-
amine such as piperazine, 2-methylpiperazine or 2,5-di-
methylpiperazine.

35   The polymeric materials utilized in the devices of

1   the present invention can be variously formed or shaped
into films, sheets, coatings, layers, fibrils, fibres or
the like. For example, a solution of a substituted poly-
amide as described hereinbefore, in a solvent material such
as N,N-dimethyl-acetamide, optionally containing lithium
5   chloride solubilizing agent, can be readily cast onto a
suitable support material for the formation of a polymeric
film or layer of the polyamide material. The polymeric film
can be utilized for the production of a birefringent poly-
meric film or sheet material which can be utilized in an
10   optical device of the invention. Thus, a polymeric film or
sheet material can be subjected to stretching so as to
introduce molecular orientation and provide a film material
having a highly birefringent character.

15   Known shaping or forming methods can be utilized for the
orientation of polymeric materials suited to application
in devices of the present invention. Preferably, this will
be accomplished by unidirectional stretching of a poly-
meric film, by extrusion of the polymer into a sheet,
20   layer or other stretched form, or by the combined effects
of extrusion and stretching. In their oriented state, the
polymers utilized herein exhibit unusually high bire-
fringence. In general, greater birefringence will be ob-
served in the case of polymeric materials exhibiting a
25   greater degree of molecular orientation. It will be
appreciated, however, as has been pointed out hereinbefore,
that the particular molecular structure or configuration of
the polymeric material may affect desired physical
attributes of the polymer material or otherwise impose a
30   practical limitation upon the degree of orientation that
can be realized by stretching or other means. It is a
significant aspect of the present invention, however, that
the polymeric birefringent materials utilized in the
devices of the present invention, particularly for a given
35   degree of orientation, exhibit unusually high birefringence.

1 In this connection, it is to be noted, for example, that
the substituted polyamides described herein will often ex-
hibit higher birefringence than the more highly oriented
materials of different polymeric structure. For example,
an extruded film of a substituted polyamide hereof
5 comprised of recurring units of the formula

10
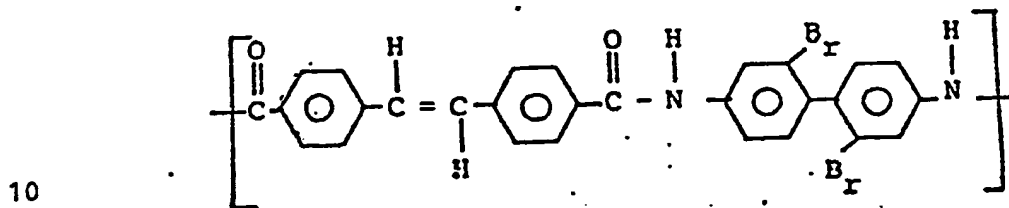
and having a degree of orientation in the range of from
about 80 % to 85 % as determined from infra-red dichroism,
15 exhibited a birefringence (Δ n) of 0.865 as measured
utilizing principles of interferometry. In contrast, a
polyamide fibre material and comprised of recurring units
of the formula:

20
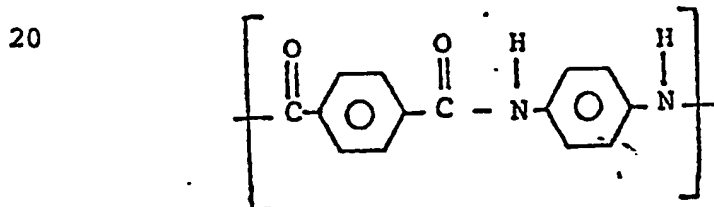
25

is reported in the literature, A.A. Hamza and J. Sikorski,
J. Microscopy, 113, 15 (1978), as having a birefringence
of 0.761, as measured by interferometric technique and at a
degree of orientation of about 90 % to 95 %.

30
The birefringent polymers useful in the devices hereof will
desirably simulate to the maxiumum practical extent the
optical properties of a uniaxial crystal. Accordingly, the
birefringent polymers will exhibit substantially uniaxial
35 optical behaviour, i.e., only two indices of refraction.

1   Optical efficiency and maximum birefringence will be
     realized where such substantially uniaxial behaviour is
     exhibited by such polymers.

     The molecularly oriented birefringent polymers utilized
5   herein will preferably exhibit a birefringence of at least
     about 0.2, and more desirably, a birefringence of at least
     0.4. Thus, preferred polymers for use in the articles
     hereof will exhibit substantially uniaxial optical behaviour
     and a birefringence of at least about 0.2 and will be
10   comprised of recurring units having a geometric index of
     about 0.5 or higher.

     The birefringent polymeric materials utilized in the
     devices of the present invention, in addition to exhibit-
15   ing high birefringent properties, are advantageous from
     the standpoint of their transparency. In contrast to poly-
     meric materials which become decidedly opaque as a result
     of stretching, birefringent materials hereof exhibit
     transparency in unoriented and stretched forms. For example,
20   the substituted polyamides described herein exhibit a high
     transparency and a low order of light scattering, exhibit-
     ing a ratio of amorphous to crystalline material of from
     about 10:1 to about 20:1 by weight. These materials are,
     thus, suited to optical applications where a light-trans-
25   missive, highly refractive and birefringent material is
     desirably utilized. Depending upon the nature of sub-
     stituent moieties on the divalent radicals of the re-
     curring units of these polyamides, colourless or nearly
     colourless polymeric films or layers can be fabricated.
30   Where, for example, nitro-substituted biphenylene radicals
     are present, a yellow transparent film or fibre can be
     fabricated. Films, coated or other shaped forms of the
     substituted polyamides can be redissolved and reshaped or
     refabricated if desired. Depending upon the nature of
35   particular recurring units of the polyamide materials,

1 and particularly the nature of substituent moieties and solvent materials, the solubility characteristics of these substituted polyamides can be varied or controlled to suit particular applications.

5 The birefringent properties of polymers utilized in the devices of the present invention can be determined by the measurement of physical and optical parameters in accordance with known principles of physics and optics. Thus, for example, the birefringence (Δn) of a suitable bire-

10 fringent polymeric material can be determined by the measurement of optical phase retardation (R) and film thickness (d) and calculation of birefringence in accordance with the relationship

$$\Delta n = \frac{R \lambda}{d}$$

15

where λ represents the wavelength of light utilized for the conduct of the measurements. Alternatively, parallel refractive index and perpendicular refractive index of the

20 film material can be measured utilizing Becke line analysis or critical angle measurement.

A preferred method for determining the birefringence of useful polymeric materials involves the measurement of

25 retardation of the polymeric material by a method utilizing principles of polarized-light microscopy and interferometry. Such method provides desired precison and accuracy in the measurement of the phase difference between a sample ray passing through a sample of polymeric material and a

30 reference ray passing through a neighbouring empty area (embedding medium or air) of the same thickness. The light emitted by a low-voltage lamp of a microscope is linearly polarized by passage through a polarizer and, in turn, is passed through a condenser, a calcite plate beam

35 splitter, a half-wave retarder plate, the polymeric sample,

1 a beam recombinator calcite plate, and through an
analyzer whose transmission direction is vertical to that
of the polarizer (crossed position). In the analyzer the
components vibrating in its absorption direction are ex-
tinguished, whereas the components of both rays in the

5 transmission direction are transmitted and interfere. The
phase difference between sample and reference beams, caused
by the molecular structure or configuration of the poly-
meric sample, is measured with compensators. From these
measurements, the thickness and refractive index of the

10 polymeric material can be determined. By determining index
of refraction of the polymeric sample for both parallel and
perpendicular directions, birefringence can, by difference,
be determined. A suitable method and apparatus for determ-
ining phase retardation, index of refraction and bire-

15 fringence for the polymeric materials utilized herein is
a pol-interference device according to Jamin-Lebedeff
described in greater detail by W.J. Patzelt, "Polarized-
light Microscopy," Ernst Leitz GmbH, Wetzlar, West Germany,
1974, page 92.

20

Preferred optical devices of the present invention are
multilayer devices which include a layer of molecularly
oriented and highly birefringent polymeric material as
described hereinbefore, and in addition, at least one

25 layer of isotropic or birefringent material. The additional
layer or layers whether isotropic or birefringent,
comprises a material having an index of refraction matching
substantially one index of refraction of the highly bire-
fringent material. For example, a layer of isotropic

30 material having an index of refraction matching substant-
ially one index of refraction of the highly birefringent
layer can be suitably bonded to the layer of highly bire-
fringent polymer. A preferred device comprises a layer of
the molecularly oriented and highly birefringent material

35 bonded between two layers of isotropic material, the index

1 of refraction of each isotropic layer constituting sub-
stantially a match with an index of refraction of the
molecularly oriented and highly birefringent material.
Such preferred device can be utilized for the polarization
of light and may be termed a "total transmission" light
5 polarizer, i.e., one which is particularly adapted to
polarize a very large portion of incident light. Total
polarizers find application in equipment such as may be
employed for signaling, projection and display purposes,
or the like, and in anti-glare systems for automotive
10 vehicles.

According to another embodiment of the present invention,
a molecularly oriented and highly birefringent material as
defined herein can be suitably bonded to an additional
15 layer of birefringent material. In such an embodiment, one
index of refraction of the molecularly oriented and highly
birefringent material will match substantially one index of
refraction of the additional birefringent material. Similar-
ly, the second index of refraction of the molecularly
20 oriented and highly birefringent material will be sub-
stantially a mismatch with respect to the second index of
refraction of the additional birefringent material. Where
a layer of molecularly oriented and highly birefringent
material is bonded to an additional layer of birefringent
25 material, the direction of orientation of each contiguous
birefringent material will be substantially perpendicular
with respect to the other.

According to another embodiment of the present invention,
30 a plurality of alternating isotropic and birefringent
layers can be utilized for the production of a multilayer
light polarizing device, at least one of the layers of
birefringent material comprising a molecularly oriented
and highly birefringent material as defined herein. Such a
35 device can be utilized as a multilayer polarizer which

1 partly transmits and partly reflects incident light as
separate linearly polarized components vibrating in ortho-
gonal directions.

In Fig. 5 is shown, in considerably exaggerated dimensions,
5 an optical device of the present invention in the form of
light-polarizing sheet material 10 as it would appear in
cross-section, namely, as viewed along a given edge. In
order of arrangement with respect to the direction of a
collimated beam 12 from a light source (not shown) the
10 material is composed of an isotropic, or at least function-
ally isotropic layer 14 having a releatively low refractive
index, a molecularly oriented highly birefringent polymeric
layer 16 and a functionally isotropic layer 18 having a
relatively high refractive index, the layers preferably be-
15 ing laminted or bonded together to form a unitary structure.
It is not essential to the proper functioning of the device
that the layers thereof be bonded together, provided, how-
ever, that adjacent or contiguous layers enclosing an air
layer are maintained paralled to one another. One refract-
20 ive index of the polymeric molecularly oriented and highly
birefringent layer 16 matches substantially that of
layer 14 while the other refractive index thereof matches
substantially the index of refraction of layer 18. For
purposes of illustration, the aforesaid refractive indices
25 may be taken as follows: the refractive index of layer 14
is 1.50; the two indices of layer 16 are 2.00 and 1.50;
and the index of layer 18 is 2.00.

The interface between layers 14 and 16 is composed of a
30 plurality of lens-like or lenticular elements 16a and the
interface between layers 16 and 18 is composed of a
plurality of lens-like or lenticular elements 16b. It will
be noted that the lenticules of one interface are offset,
laterally, with respect to those of the other. The term
35 "lenticular", as employed herein, may broadly be inter-

1 preted as constituting a plurality of surface configurations,
including prismatic elements, as well as those of a strictly
lens-like form. A certain degree of latitude is possible as
to the choice of materials employed in forming the several
layers. Thus, for example, layer 14 may suitably be composed
5 of an isotropic plastic material such as poly(methylmeth-
acrylate) having a refractive index of 1.50. Layer 16 can,
accordingly, be composed of a transparent plastic layer which
for example, has been rendered birefringent as by unidirect-
ional stretching. Suitable for this purpose is the polymeric
10 material, poly[2,2'-bis(trifluoromethyl)-4,4'-biphenylene] 2",
2'"-dimethoxy-4,4'"-biphenyldicarboxamide having refractive
indices of 1.50 and 2.00 when thus rendered birefringent.
Layer 18 can be suitably comprised of or incorporate a trans-
parent isotropic material having an index of refraction
15 approximating the higher index of birefringent layer 16.

One such material is poly(2,2'-dibromo-4,4'-biphenylene)-
4",4"'-stilbenedicarboxamide having an index of refraction
of 2.07. Alternatively, layer 18 can comprise poly(2,2'-di-
20 bromo-4,4'-biphenylene)-α-bromo-4",4"'-stilbenedicarbox-
amide having a refractive index of 2.05.

One method of constructing the sheet material is to form the
birefringent layer 16 by a casting, or a casting and
25 embossing procedure, after its proper solidification, and
casting the isotropic layers 14 and 18 on the opposite
lenticular surfaces thereof. The birefringent layer 16 may
be composed of substantially any material having a bire-
fringence adapted to facilitate the required separation of
30 light ray components and having indices of refraction which
bear a proper relation to those of the contiguous layers 14
and 18. It may also be formed by any of several different
procedures. Assuming, by way of illustration, that the bi-
refringence of layer 16 is to be achieved through its
35 molecular orientation, a sheet or film of properly deform-

1 able material, such as the aforementioned material,
poly[2,2'-bis(trifluoromethyl)-4,4'-biphenylene]-2",2"'-
dimethoxy-4",4"'-biphenyldicarboxamide, i.e. a sheet of a
given length and predetermined thickness, can be first
extruded or cast. The sheet can then be subjected to a
5 mechanical stress in a longitudinal direction to elongate
and molecularly orient it, as by a stretching operation in
the presence of heat or other softening agent, or by a cold
drawing method, or, again, by applying amechanical stress
to its surface. The direction of stretch or other applicat-
10 ion of orienting stress is to be taken as having been per-
formed toward and away from the viewer, namely, in a
direction normal to the plane of the paper. This being the
case, the optic axis 20 of layer 16 constitutes a direction
both in the plane of layer 16 and normal to the plane of the
15 paper.

Birefringent layer 16, having acquired the desired bire-
fringence as, for example, a birefringence of 1.50 and 2.00,
assuming the stated refractive indices, can then be sub-
20 jected to surface modification to form thereon the converg-
ing or positive lenticular elements 16a and the diverging
but functionally converging or positive lenticular ele-
ments 16b. This can be suitably performed by passing the
material between embossing means such as embossing blades,
25 wheels or the like, the surfaces being slightly softened as
by a solvent or heat, or both, as may be necessary during
their treatment but not to such an extent as would relax
the material and alter the previously provided orientation
and birefringence. The embossing procedure is preferably
30 performed in a direction along that of the optic axis, to
facilitate preservation of the given orientation. Accord-
ingly, the lenticules, as illustrated, are generally
cylindrical with their axes extending parallel to the
optic axis. As will be apparent and explained in further
35 detail below, the lenticules play a major role in the

1 predetermined separation and focusing of the respective
rays. While lenticular means of the type described con-
stitute one preferred configuration, they may be so formed
as to extend in other directions of the sheet or even have
a spherical shape, provided that their refractive
5 characteristics are properly chosen and the birefringence
of the material is suitable. Alternatively, the lenticules
may be formed by a grinding and polishing procedure or the
sheet may be stretched or otherwise treated for orienting
its molecules after the lenticules have been formed thereon.
10
After completion of the surfacing of the birefringent
layer 16 and either prior to or after its orientation, the
isotropic layers 14 and 18 are assembled therewith or formed
thereon by any appropriate method such as by casting them
15 in liquid form on the preformed layer 16. Assuming that the
material of layers 14 and 18 is not of a type to cause any
disturbing double refraction of light rays when solidified
and subjected to mechanical stress, as by stretching, the
stretching and desired molecular orientation of layer 16
20 may be accomplished after casting and solidifying layers 14
and 18 on its surfaces, the entire sheet 10 then being
stretched as a unit. Or, the layers 14 and 18 may be cast
on layer 16 after orientation of the latter. Alternatively,
and again assuming layers 14 and 18 to be substantially
25 incapable of becoming birefringent when stressed, they may
be preformed so as to have the lenticular surfaces shown,
superimposed in correctly spaced relation, the bire-
fringent layer 16 formed therebetween in a fluid state and
solidified, and the entire unit then stretched. In a further
30 modification, the layers 14 and 18 may be preformed and
assembled with layer 16, in either a bonded or non-bonded
relation therewith, after the layer 16 has been treated to
acquire a proper birefringence.

35 It has been noted with reference to Fig. 5, that the

1 lenticules 16a and 16 b are relatively offset from left to
right, that is transversely of the sheet 10, so that the
vertices of lenticules 16a are optically aligned with the
longitudinal edges or intersections of lenticules 16b.
While the lenticules 16a and 16b are shown as being
5 spherical and of similar radii of curvature it will be
understood that neither of these conditions is essential,
per se, the choice depending in general upon the direction
in which the rays are required to be refracted, the extent
of their travel in said directions, and such factors as the
10 refractive indices and thicknesses of the layers.

The collimated beams 12, emanating, for example, from a
light source and reflector of a headlamp (not shown) and
normally incident upon the isotropic layer 14, are trans-
15 mitted without deviation through the latter to the converg-
ing cylindrical lenticules 16a of birefringent layer 16.
At layer 16 each beam is resolved into two components, that
is an ordinary or "O" ray 12a and an extraordinary or "E"
ray 12b. Bearing in mind that the refractive index of
20 isotropic layer 14 has been given as 1.50 and the refractive
indices of birefringent layer 16 as 1.50 and 2.00 let it be
assumed that the 1.50 refractive index applies to the
components 12a which, for purposes of illustration, will be
considered the ordinary rays vibrating substantially at
25 right angles to the optic axis. Inasmuch as these rays have
a refractive index which is essentially identical to that
of layer 14, which precedes layer 16 in order of their
travel, they are refracted by lenticules 16b so to converge
generally toward a theoretical focal plane, not shown. The
30 rays 12a pass through isotropic layer 14 without deviation
inasmuch as the refractive index of 1.50 and that of
layer 14 are substantially identical. The components 12b,
which in this instance are taken as the extraordinary rays
vibrating in a plane passing through or parallel with the
35 optic axis and having a refractive index of 2.00 identical

1 to that of the isotropic layer 18, are refracted by the
lenticules 16a because of the dissimilarity of respective
refractive indices. However, the diverging or negative
lenticular surface 16a constitutes, in effect a converging
lenticular surface of isotropic layer 14, the components 12b
5 thereby being refracted convergently toward the aforesaid
theoretical focal plane. As described, the layer 16 is
positively birefringent inasmuch as the refractive index
of the E ray is represented as greater than that of the
O ray, but a reverse condition is possible. The rays 12a
10 and 12b, generated in birefringent layer 16 are plane
polarized, their vibration directions being at 90° to one
another as indicated. The rays are thence transmitted without
alteration of their state of polarization with their vibr-
ational planes normal to one another.

15
Either the E or the O ray, or both, may be selectively
treated, as by passing them through retardation materials,
to provide their vibrations in a single azimuth as will be
described below. Even without such treatment and a non-
20 uniformity of vibration directions, the sheet material of
Fig. 5 has certain uses such, for example, as for
illumination purposes where it is desired to polarize the
light partially in a given direction; for three-dimensional
viewing or for any function wherein transmission of a large
25 part of the incident light is of importance but wherein
completely uniform polarization throughout a given area is
not essential. While the entering rays 12 are shown as
collimated at 90° to the plane of the sheet, a slight
departure from this condition, from left-to-right in the
30 drawing, can exist without preventing operation of the
device of Fig. 5 or of others illustrated herein and a wide
deviation therefrom may exist in a direction along the
axis of the lenticules.

35 Consistent with obtaining an operational refraction or non-

refraction of rays generally similar to that shown in Fig. 5, the several layers may be formed of substantially any materials having suitable refractive indices, transparency and physical or mechanical properties such as thermal stability, flexibility or adhesion. Thus, for example, layer 14 may be composed of any of such materials as tetrafluoroethylene, vinyl acetate, cellulose acetate butyrate, an acrylic material, glass or the like. Birefringent layer 16 can be, for example, poly[2,2'-bis(trifluoromethyl)-4,4'-biphenylene]-4",4"'-stilbenedicarboxamide having indices of refraction 1.61 and 2.48 or a layer of poly(2,2'-dibromo-4,4'-biphenylene)-4",4"'-stilbenedicarboxamide having indices of 1.77 and 2.64. Layer 18 can be a polymeric material which has been rendered birefringent but which has its optic axis or direction of molecular orientation at 90° to that of layer 16, it being understood that its lenticular surface would match with that of layer 16 at 16b.

In an optical device of the present invention, the indices of refraction of the several layers can be modified or adjusted in predetermined manner such that the proper functional relation beween the indices of refraction of the several layers is maintained. Thus, the indices of refraction of the several layers may be controlled in predetermined fashion by altering plasticizer content. For example, the index may be lowered by the addition of plasticizer. Where bonding substances or subcoats are employed in laminating preformed layers, a material used for such a purpose should have an index of refraction similar to that of one of the layers undergoing bonding to prevent unwanted reflection.

According to another embodiment of the present invention there is provided a light-polarizing element comprising a prismatic layer of molecularly oriented birefringent material and an isotropic or functionally isotropic layer.

1 Such an element can be utilized in a device such as the headlamp of an automotive vehicle.

In Fig. 6 there is shown a headlamp 30 which includes a specularly reflecting parabolic mirror 32, a filament 34,
5 a diffusely reflecting plate element 36 and a light-polarizing sheet material 40. Light-polarizing element 40 includes a prismatic layer 42 of molecularly oriented and highly birefringent polymer and an isotropic layer 44, the refractive index of the isotropic layer 44 substantially
10 matching the low index of refraction of birefringent layer 42. Thus, for example, birefringent layer 42 may have refractive indices of 2.00 and 1.50 and layer 44 a refractive index of 1.50. An unpolarized collimated beam 12, upon entering birefringent layer 42, is resolved into O and E
15 components 12a and 12b, as previously described in connection with the device shown in Fig. 5. The prism elements of birefringent layer 42 are so formed and disposed relative to the incident collimated beam 12 that the E ray 12b is reflected rearwardly to the parabolic mirror 32, is
20 reflected to. diffusely reflecting element 36, whereat it is depolarized, is reflected to mirror 32 and thence to light-polarizing sheet material 40 as a second collimated unpolarized beam 12d. The prism elements, may for this purpose, appropriately be prisms or so-called hollow corner
25 cubes which have the characteristic of reflecting collimated light rays in the direction whence they came. The O ray 12a is transmitted without deviation straight through layer 44 which matches its refractive index. This procedure repeats itself, ad infinitum, it being apparent that
30 eventually subsantially all of the light from source 34 is transmitted in the form of collimated O rays having a uniform azimuth of polarization.

According to still another embodiment of the present invention, there is provided a multilayer light-polarizing
35

1 device effective to linearly polarize a large portion of
the light incident thereon and to transmit substantially
all of one polarized component of light while reflecting
substantially all of the orthogonally polarized component.
Such a polarizer is shown in Fig. 7 as polarizer 50 having

5 alternate layers 54 and 56 of molecularly-oriented, highly-
birefringent material and of isotropic or functionally iso-
tropic material.

The layers 54 are each composed of a molecularly oriented

10 birefringent material. For instance, the material may
comprise poly[2,2'-bis(trifluoromethyl)-4,4'-biphenylene] 2",
2"'-dimethoxy-4",4"'-biphenyldicarboxamide. Other materials
can also be utilized in forming the birefringent layer and
should be selected to have as great a difference between the

15 two indices of refraction as possible since the number of
layers in the polarizer can be substantially decreased when
using birefringent materials having a greater difference
between their indices of refraction.

20 The isotropic layers 56 may be composed of a number of
different materials with the requirement that its refract-
ive index substantially match one of the refractive indices
of the birefringent material layers on either side thereof.
Some examples of materials which are useful for this

25 purpose include polyacrylates, poly(2,2'-dibromo-4,4'-bi-
phenylene)4",4"'-stilbenedicarboxamide, silicon oxides or
titanium dioxides. The isotropic layers can be provided,
for example, by vacuum deposition so that their thickness
can be precisely controlled. Alternately, the isotropic

30 layer may be co-extruded simultaneously with the birefringent
layers interleaved therebetween.

As shown in Fig. 7 the optical axis 58 of each birefringent
layer lies in a plane parallel to the planar substrate

35 surface 60. This is accomplished, for example, through the

1   use of a stretch orientation operation. Layer thickness
can be suitably controlled by the extrusion process and
allowances for dimensional changes expected in the layer
thickness during the stretching step can be made.

5   Fig. 7 schematically shows a number of light rays 62 in-
cident on polarizer 50 and traveling in a direction per-
pendicular to the surface thereof. As an example, the bi-
refringent layers 54 may have a pair of refractive indices
of $n_O = 1.50$ and $n_E = 2.00$ and the refractive index of each
10   isotropic layer may be taken as n = 1.50. As each ray 62
passes through the first birefringent layer 54, it is
resolved thereby into two components shown as separate
rays, namely, an extraordinary or "E" ray 62a for which the
birefringent layer has the higher index $n_E = 2.00$ and an
15   ordinary ray or "O" ray 62b for which the birefringent laye
has, for example, the lower index $n_O = 1.50$, the rays
traveling in a similar direction and with their vibration
azimuths relatively orthogonally disposed as depicted in
the drawing. As shown in Fig. 7, a portion 62c of the "E"
20   rays 62a is reflected at the first interface 64 reached, it
being recalled that the refractive index of an isotropic
layer was given at n = 1.50. The reflection is due to the
refractive index discontinuity at the interface between the
layers 54 and 56 which exists for the "E" polarization but
25   not the "O" polarization. For purposes of illustration the
reflected light rays 62c are shown as being reflected at a
slight angle while in actuality they are reflected straight
back in the direction of rays 62a. Thereafter each interface
such as 66 and 68 will reflect a further portion of ray 62a.
30   The rays 62b are unreflected at the interface 64 because
the refractive index for "O" rays 62b in layer 54 matches
that of layer 56 and in fact, these rays 62b will pass
through all layers 54 and 56 unreflected and comprise that
portion of the light incident on the polarizer that is
35   transmitted thereby.

1   In order to greatly increase the reflectivity of the
     polarizer 50 each layer 54 and 56 is made to have an
     optical thickness of one-quarter the length of a selected
     wavelength. The optical thickness is equal to the physical
     thickness multiplied by the index of refraction of the
5   layer material. The wavelength selected is preferably in
     the middle of the visible spectrum, for example, 550 nm so
     that the polarizer is effective over a substantial range of
     visible light. This arrangement utilizes optical inter-
     ference to enhance the efficiency of the polarizer. The
10   following discussion relates to phase changes in a light
     wave, not to changes in the polarization azimuth of the
     light wave. In alalyzing the optical properties of the
     polarizer, it is important to remember that light suffers a
     phase change of π on reflection when it goes from a medium
15   of low refractive index to a medium of higher refractive
     index while it suffers no phase change on reflection when
     it goes from a medium of high refractive index to a medium
     with a lower refractive index. Thus, in Fig. 7, a light
     ray such as 62a, as it passes through the first quarter-
20   wave birefringent layer 54 will suffer a phase change $\pi/2$.
     As the light ray strikes the first interface 64 part of it
     is reflected back through the first birefringent layer 54
     again suffering a phase change of $\pi/2$, the total phase
     change being equal of $\pi/2 + \pi/2 = \pi$. Note that the ray 62a
25   suffers no phase change on reflection at interface 64 due
     to the rule as stated above. Now as the remaining portion of
     ray 62a strikes the second interface 66, it has traveled
     through two layers suffering a phase change of $\pi/2 + \pi/2$
     in one direction and $\pi/2 + \pi/2$ on reflection. The ray 62a
30   will also suffer a phase change of π on reflection due to
     the above rule and the total phase change will equal
     $4\pi/2 + \pi$ or 3π. Thus, in accordance with this analysis,
     the ray 62a will always suffer a phase change of some
     multiple of π as it is reflected from each and every inter-
35   face in the multilayer polarizer. Each reflected

1 component 62c of ray 62a and other such similar rays will
reinforce one another resulting in substantially total
reflection of the one polarized component of incident
light represented by ray 62a providing the number of layers
and interfaces are sufficient. The other component 62b

5 will pass undisturbed through the multilayer polarizer 50
so long as the refractive index of the isotropic layers 56
match one of the refractive indices of the birefringent
layers 54. Since substantially none of the rays 62a are
transmitted, the entire amount of light output from

10 polarizer 50 consists of rays 62b, all polarized in one
direction.

In Fig. 8 is shown an optical beam-splitter device of the
present invention embodying a layer of birefringent poly-

15 mer. Beam splitter 70 comprises prisms 72a and 72b of iso-
tropic material such as glass joined in a Nicol configurat-
ion with a layer 74 of molecularly oriented birefringent
polymer therebetween. Elements 72a and 72b can be composed
of a variety of glass or other isotropic materials and

20 will have a perpendicular index of refraction greater than
that of the polymer layer 74 between such elements. For
example, a unidirectionally stretched layer 74 of poly-
[2,2'-bis(trifluoromethyl)-4,4'-biphenylene]-2,2'-dimethoxy-
4,4'-biphenyl having a perpendicular index of refraction of

25 about 1.65 and a unidirectional stretch direction as
indicated in Fig. 8 can be utilized between isotropic glass
elements 72a and 72b of refractive index 1.8. In operation,
unpolarized light 76 enters element 72a and a portion
thereof is reflected at the interface of element 72a and

30 layer 74 so as to emerge as plane-polarized light 78. A
portion of light 76 is refracted by layer 74 and emerges
from element 72b as oppositely plane-polarized light 80.
Light 76 is thus split into separate beams of oppositely
polarized light by beam splitter 70.

35

1   While particular embodiments of the present invention
utilizing polymeric birefringent layers have been described
in connection with the devices shown in Figs. 5 to 7,
other devices utilizing such polymeric birefringent layers
can also be prepared. Examples of other devices which can

5   be adapted to inculde a polymeric and highly birefringent
layer as described herein are described, for example, in
U.S. Patent 3,506,333 (issued April 14, 1970 to E.H. Land);
in U.S. Patent 3,213,753 (issued October 26, 1965 to H.G.
Rogers); in U.S. Patent 3,610,729 (issued October 5, 1971

10   to H.G. Rogers); in U.S. Patent 3,473,013 (issued
October 14, 1969 to H.G. Rogers); in U.S. Patent 3,522,984
(issued August 4, 1970 to H.G. Rogers); in U.S. Patent
3,522,985 (issued August 4, 1970 to H.G. Rogers); in U.S.
Patent 3,528,723 (issued September 15, 1970 to H.G. Rogers);

15   and in U.S. Patent 3,582,424 (issued June 1, 1971 to K.
Norvaisa). Still other devices that can be prepared
utilizing a birefringent polymer hereof include Wollaston
prisms, Rochan prisms, Fuessner prisms, Brewster polarizers,
non-polarizing beam splitters, compensators and the like.

20

The following non-limiting examples are illustrative of
the present invention.

Example 1

25

This example illustrates the preparation of poly(2,2'-di-
bromo-4,4'-biphenylene)-p,p'-biphenylene dicarboxamide and
the preparation therefrom of birefringent polymeric films.

30   A 50-ml reaction vessel (a resin-making kettle equipped with
a mechanical stirrer, nitrogen inlet tube and calcium
chloride drying tube) was heated while simultaneously
flushing the vessel with nitrogen. After the reaction
vessel had cooled to room temperature, 1.63 g of anhydrous

35   lithium chloride and 0.5746 g (0.001679 mole) of sublimed

2,2'-dibromobenzidine were added while maintaining a positive nitrogen pressure. The reaction vessel was fitted with a thermometer and a rubber stopple (a rubber membrane-like sealing lid capable of receiving a syringe and of sealing itself upon removal of the syringe). 10 ml of anhydrous distilled N-methylpyrrolidone (NMP) and 15 ml of anhydrous distilled tetramethylurea (TMU) were carefully added with the aid of syringes. The resulting mixture was stirred and warmed to 40°C until all solids had dissolved. The solution was then cooled in a bath of ice and salt to a temperature of -5°C. A small amount of lithium chloride precipitation was observed. Recrystallized p,p'-biphenylene dicarbonyl chloride (0.4689 g; 0.001679 mole) was quickly added by means of a funnel to the stirred 2,2'-dibromo-benzidine solution. An additional 5 ml of TMU were added through the funnel to the reaction mixture. The temperature of the reaction mixture did not rise above a temperature of 7°C. After stirring for 60 minutes, the reaction mixture began to thicken and streaming brefringence (but not stir opalescence) was observed.

The ice bath was removed from the reaction vessel and the temperature was observed to rise to 20°C in 30 minutes at which point the reaction solution became milky in appear-ance. The reaction vessel was placed in an oil bath (40°C) and the reaction mixture was warmed for 30 minutes. The reaction mixture became clear. The temperature of the reaction mixture rose during the warming to a maximum temperature of 55°C at which temperature the reaction mixture was stirred for 1 hour. The reaction product, a 3 % wt./vol. polymer solution (3 g of polymer per 100 ml of reaction solvent) was cooled to 40°C and poured into 200 ml of ice-water in a blender. The resulting fibrous solid was filtered and washed (in the blender) twice each with water, acetone and ether. The product was dried in a vacuum oven at 15 mm pressure and 90°C for 18 hours. The

1 product, obtained in 95.4 % yield, was a white fibrous
polymeric material having the following recurring
structural units:

5
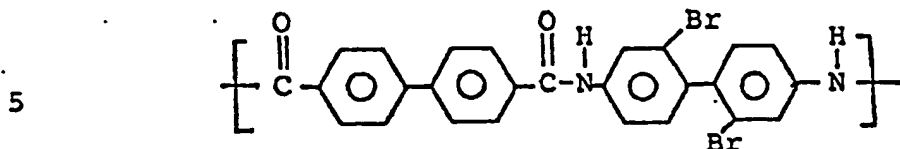
The inherent viscosity of a polymer solution (0.5 g of the
10 polymer of Example 1 per 100 ml of a solution of 5 g
lithium chloride per 100 ml of dimethylacetamide) was
3.54 dl/g at 30°C.

Molecular structure was confirmed by infrared spectroscopy.
15 Inspection of the ultraviolet/visible absorption spectrum
for the polymer of Example 1 (in 5 % wt./vol. lithium
chloride/dimethylacetamide) showed a λ_{max} of 320 (ε = 75,000).

Elemental analysis for $C_{26}H_{16}Br_2N_2O_2$ provided the following:

20

	%C	%H	%Br	%N	%O	
Calculated:	56.97	2.92	29.16	5.11	5.84	
Found:	56.86	3.25	28.72	5.10	6.07	(by difference)

25 Polymeric films were prepared from the polymeric material of
Example 1 by casting (onto glass plates) solutions of the
polymeric material in a 5 % wt./vol. solution of lithium
chloride and dimethylacetamide (5 g lithium chloride per
100 ml of dimethylacetamide). The concentration of polymer
30 ranged from 0.5 to 5 % wt./vol., i.e., from 0.5 g to 5 g
polymer per 100 ml of the lithium chloride/dimethylacetamide
solution. In each instance, the glass plate carrying the
puddle-cast polymer solution was immersed in water (after
minimal evaporation of solvent). The polymer film was ob-
35 served to gel and a transparent and colourless unoriented

film separated from the glass plate. The resulting film was soaked for several hours in water to effect extraction of occluded lithium chloride and solvent, soaked in acetone and dried in a vacuum oven at 90°C and 15 mm pressure. Refractive index, measured by interferometry, was 1.93,

Stretched polymeric films were prepared in the following manner. Water-swollen films (obtained by soaking the polymer films for several hours for removal of occluded lithium chloride and solvent as aforedescribed) were cut into strips. The strips were mounted between the jaws of a mechanical unidirectional stretcher. The strips were stretched (in air at 220°C) to about 50 % elongation, to effect film orientation. The resulting films were optically transparent. Birefringence, measured with the aid of a quartz wedge, was 0.293.

Example 2

This example illustrates the preparation of poly(2,2'-dinitro-4,4'-biphenylene)-o,o'-dinitro-p,p'-biphenylene dicarboxamide and the preparation therefrom of birefringent polymeric films.

A 50 ml reaction vessel (a resin-making kettle equipped with a mechanical stirrer, nitrogen inlet tube and calcium chloride drying tube) was heated while simultaneously flushing the vessel with nitrogen. After the reaction vessel had cooled to room temperature, 1.5 g of anhydrous lithium chloride and 0.4799 g (0.001750 mole) of recrystallized 2,2'-dinitrobenzidine yellow crystals were added while maintaining a positive nitrogen pressure. The reaction vessel was fitted with a thermometer and a rubber stopple and 30 ml of anhydrous distilled N-methylpyrrolidone (NMP) and 20 ml of anhydrous distilled tetramethylurea (TMU) were carefully added with the aid of syringes.

1 The resulting mixture was stirred and warmed to 40°C until
all solids had dissolved. The solution was then cooled in a
bath of ice and salt to a temperature of -5°C. Recrystalliz-
ed colourless 2,2'-dinitro-4,4'-biphenyl dicarbonyl
chloride (0.6460 g; 0.00175 mole) was quickly added by
5 means of a funnel to the stirred 2,2'-dinitrobenzidine
solution. An additional 3 ml of NMP were added through the
funnel to the reaction mixture. The temperature of the
reaction mixture did not rise above a temperature of 0°C.
After stirring for 30 minutes, there was no noticeable
10 change in reaction mixture viscosity.

The ice bath was removed from the reaction vessel and the
temperature was observed to rise to 20°C in 30 minutes at
which point the reaction solution was heated in stages up
15 to 90°C over a period of 2.5 hours.

The reaction product, a 3 % wt./vol. polymer solution
(3 g of polymer per 100 ml of reaction solvent) was cooled
to 40°C and poured into 200 ml of ice-water in a blender.
20 The resulting gelatinous solid was filtered and washed (in
the blender) twice each with water, acetone and ether. The
product was dried in a vacuum oven at 15 mm Hg pressure and
90°C for 18 hours. The polymeric product, obtained in 88 %
yield, was a dark-yellow powder having the following re-
25 curring structural units:
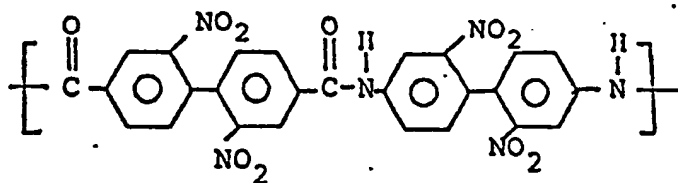
30

The inherent viscosity of a polymer solution (0.5 g of the
polymer of Example 2 per 100 ml of a solution of 5 g
lithium chloride per 100 ml of dimethylacetamide) was
35 1.40 dl/g at 30 °C.

Molecular structure was confirmed by infrared spectroscopy. Inspection of the ultraviolet/visible absorption spectrum for the polymer of Example 2 (in 5 % wt./vol. lithium chloride/dimethylacetamide) showed a λ_{max} of 307 nm ($\mathcal{E}$ = 38,400) and an absorption peak at 365 nm ($\mathcal{E}$ = 3,000).

Elemental analysis for $C_{26}H_{14}N_6O_{10}$ provided the following:

	%C	%H	%N	%O
Calculated:	54.74	2.47	14.73	28.06
Found	54.24	2.60	13.91	29.25 (by difference)

Thermogravimetric analysis showed that onset of degradation of the polymer of Example 2 occurred at 360°C in nitrogen and at 300°C in air. Differential scanning calorimetry and thermal mechanical analysis of film samples showed a reproducible transition at about 190°C.

Polymeric films were prepared from the polymeric material of Example 2 by casting (onto glass plates) a solution of the polymeric material in a 5 % wt./vol. solution of lithium chloride and dimethylacetamide (5 g lithium chloride per 100 ml of dimethylacetamide). The concentration of polymer was 5 % wt./vol., i.e., 5 g polymer per 100 ml of the lithium chloride/dimethylacetamide solution. In each instance, the glass plate carrying the puddle-cast polymer solution was immersed in water (after most of the solvent had evaporated). The polymer film was observed to gel and a transparent, yellow unoriented film separated from the glass plate. The resulting film was soaked for several hours in water to effect extraction of occluded lithium chloride and solvent.

Stretched polymeric films were prepared in the following manner. Water-swollen films (obtained by soaking the poly-

1   mer films for several hours for removal of occluded lithium
    chloride and solvent as aforedescribed) were cut into
    strips. The strips were mounted between the jaws of a
    mechanical unidirectional stretcher. The strips were
    stretched (in boiling ethylene glycol) to about 60 %
5   elongation, to effect film orientation. The resulting
    polymeric strips were optically transparent. Birefringence,
    measured with the aid of a quartz wedge, and by index
    matching, was 0.33. The calculated isotropic refractive
    index was 1.75. Wide-angle X-ray analysis of·the bire-
10 fringent films showed crystallinity to be less than 10 %
    by weight.

Example 3

15 This example illustrates the preparation of poly(2,2'-di-
    bromo-4,4'-biphenylene)-o,o'-dibromo-p,p'-biphenylene di-
    carboxamide and the preparation therefrom of birefringent
    polymeric films.

20 A 50 ml reaction vessel (a resin-making kettle equipped with
    a mechanical stirrer, nitrogen inlet tube and calcium
    chloride drying tube) was heated while simultaneously flush-
    ing the vessel with nitrogen. After the reaction vessel
    had cooled to room temperature, 2.0 g of anhydrous lithium
25 chloride and 0.7828 g (0.002289 mole) of sublimed 2,2'-di-
    bromobenzidine were added while maintaining a positive
    nitrogen pressure. The reaction vessel was fitted with a
    thermometer and a rubber stopple and 20 ml of anhydrous
    distilled N-methylpyrrolidone (NMP) and 35 ml of anhydrous
30 distilled tetramethylurea (TMU) were carefully added with
    the aid of syringes. The resulting mixture was stirred and
    warmed to 40°C until all solids had dissolved. The solution
    was then cooled in a bath of ice and salt to a temperature
    of 0°C. Recrystallized 2,2'-dibromo-4,4'-biphenylene di-
35 carbonyl chloride (1.0000 g; 0.002289 mole) was quickly

added by means of a funnel to the stirred 2,2'-dibromobenz-
idine solution. An additional 5 ml of TMU, at a temperature
of 25°C, were added through the funnel to the reaction
mixture. The temperature of the reaction mixture rose to
15°C and then dropped to 4°C. After stirring for 15 minutes,
the reaction mixture began to thicken and streaming bire-
fringence (but not stir opalescence) was observed. Stirring
was continued for an additional 30 minutes at 7°C and the
ice bath was removed from the reaction vessel. The temper-
ature of the reaction mixture rose to 25°C (in 90 minutes)
and the reaction mixture was then slowly heated to 100°C
over a two-hour period.

The reaction product, a 4 % wt./vol. polymer solution
(4 g of polymer per 100 ml of reaction solvent) was cooled
to 40°C and poured into 200 ml of ice-water in a blender.
The resulting fibrous solid was filtered and washed (in
the blender) twice each with water, acetone and ether. The
product was dried in a vacuum oven at 15 mm pressure and
90°C for 18 hours. The product, obtained in 96.6 % yield,
was a white fibrous polymeric material having the following
recurring structural units:
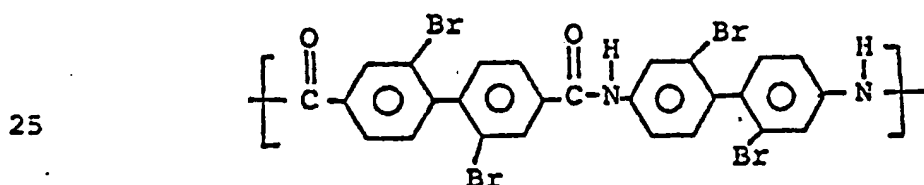
The inherent viscosity of a polymer solution (0.5 g of the
polymer of Example 3 per 100 ml of a solution of 5 g
lithium chloride per 100 ml of dimethylacetamide) was
2.04 dl/g at 30 °C. Molecular weight determination based
on light scattering, indicated 2.72×10^5, and by gel
permeation chromatography, a molecular weight of 5.66×10^4.
Molecular structure was confirmed by infrared spectroscopy.

1   Inspection of the ultraviolet/visible absorption spectrum
for the polymer of Example 3 (in 5 % wt./vol. lithium
chloride/dimethylacetamide) showed a λ_{max} of 305 nm
(ε = 31,900) and no absorption above 380 nm.

5   Elemental analysis for $C_{26}H_{14}Br_4N_2O_2$ provided the following

	%C	%H	%Br	%N	%O
Calculated:	44.23	1.99	45.27	3.99	4.52
Found:	44.54	2.19	45.25	3.87	4.15

10   Thermogravimetric analysis showed that onset of degradation
of the polymer of Example 3 occurred at 530°C in nitrogen.
Thermal mechanical analysis of film samples showed a re-
producible transition at about 120°C.

15   Polymeric films were prepared from the polymeric material
of Example 3 by casting (onto glass plates) solutions of
the polymeric material in a 5 % wt./vol. solution of
lithium chloride and dimethylacetamide (5 g lithium
20   chloride per 100 ml of dimethylacetamide). The concentratio
of polymer ranged from 0.5 to 5 % wt./vol., i.e. from 0.5 g
to 5 g polymer per 100 ml of the lithium chloride/dimethyl-
acetamide solution. In each instance, the glass plate
carrying the puddle-cast polymer solution was immersed in
25   water (after most of the solvent had evaporated). The poly-
mer film was observed to gel and a transparent, colourless
unoriented film separated from the glass plate. The result-
ing film was soaked for several hours in water to effect
extraction of occluded lithium chloride and solvent, soaked
30   in acetone and dried in a vacuum oven at 90°C and 15 mm Hg
pressure. Refractive index, measured by interferometry,
was 1.84.

Stretched polymeric films were prepared in the following
35   manner. Water-swollen films (obtained by soaking the

1   polymer films for several hours for removal of occluded
    lithium chloride and solvent as aforedescribed) were cut
    into strips. The strips were mounted for stretching between
    the jaws of a mechanical unidirectional stretcher. Strips
    were stretched, in some instances, in air at 220°C and, in
5   other instances, in boiling ethylene glycol. Elongation
    ranged from 60 % to 65 %. Infrared dichroism indicated that
    the films were less than 65 % oriented. The films were
    optically transparent. Birefringence, measured with the aid
    of a quartz wedge, was 0.390. Wide-angle X-ray analysis of
10 the birefringent polymer films showed them to be less than
   10 % by weight crystalline.

                        Example 4

15 This example illustrates the preparation of poly(2,2'-di-
    chloro-5,5'-dimethoxy-biphenylene)-o,o'-dibromo-p,p'-bi-
    phenylene dicarboxamide and the preparation therefrom of
    birefringent polymeric films.

20 A 50-ml reaction vessel (a resin-making kettle equipped with
    a mechanical stirrer, nitrogen inlet tube and calcium
    chloride drying tube) was heated while simultaneously
    flushing the vessel with nitrogen. After the reaction vessel
    had cooled to room temperature, 1.5 g of anhydrous lithium
25 chloride and 0.6519 g (0.002082 mole) of sublimed 2,2'-di-
    chloro-5,5'-dimethoxybenzidine were added while maintaining
    a positive nitrogen pressure. The reaction vessel was fitted
    with a thermometer and a rubber stopple and 10 ml of an-
    hydrous distilled N-methylpyrrolidone (NMP) and 10 ml of
30 anhydrous distilled tetramethylurea (TMU) were carefully
    added with the aid of syringes. The resulting mixture was
    stirred and warmed to 40°C until all solids had dissolved.
    The resulting orange solution was then cooled in a bath of
    ice and salt to a temperature of 0°C. A small amount of
35 lithium chloride precipitation was observed. Recrystallized

1   2,2'-dibromo-4,4'-biphenyldicarbonyl chloride (0.9095 g;
       0.002082 mole) was quickly added by means of a funnel to
       the stirred 2,2'-dichloro-5,5'-dimethoxybenzidine solution.
       An additional 10 ml of TMU (at a temperature of 25°C) were
       added through the funnel to the reaction mixture. The
5   temperature of the reaction mixture did not rise above a
       temperature of 0°C. After stirring for 30 minutes, the
       formation of a gelatinous, light-yellow, transparent mass
       (which exhibited streaming brefringence but not stir
       opalescence) was observed. Stirring was continued for an
10   additional 10 minutes at 8°C, the stirring was stopped and
       the ice bath was removed. The temperature of the reaction
       mass was observed to rise to 25°C in 15 minutes, and the gel
       became stiffer in consistency. Heating was immediately
       commenced and an additional 20 ml of TMU were added to
15   facilitate dissolution of the reaction mass. Within
       60 minutes the temperature rose to 90°C   and the gel
       melted to provide a homogeneous, viscous solution. Heating
       at 90°C was continued for two hours while stirring vigor-
       ously.

20
       The reaction product, a 2.82 % wt./vol. light-yellow poly-
       mer solution (2.82 g of polymer per 100 ml of reaction
       solvent) was cooled to 40°C and the resulting gelatinous,
       transparent mass was added to 200 ml of ice-water in a
25   blender. The resulting rubbery solid was filtered and
       washed (in the blender) twice each with water, acetone and
       ether. The product was dried in a vacuum oven at 15 mm Hg
       pressure and 90°C for 18 hours. The product, obtained in
       99.3 % yield, was a very pale-yellow fibrous polymeric
30   material having the following recurring structural units:

35
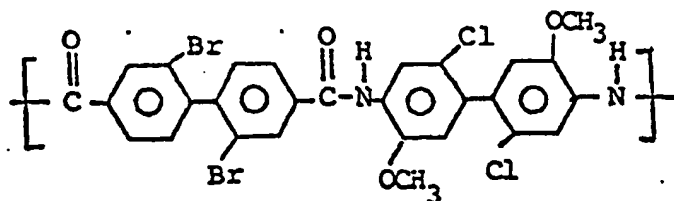
The inherent viscosity of a polymer solution (0.5 g of the polymer of Example 4 per 100 ml of a solution of 5 g lithium chloride per 100 ml of dimethylacetamide) was 5.75 dl/g at 30°C.

Molecular structure was confirmed by infrared spectroscopy. Elemental analysis for $C_{28}H_{18}Br_2Cl_2N_2O_4$ provided the following:

	%C	%H	%Br	%Cl	%N	%O
Calculated:	49.66	2.68	23.60	10.47	4.14	9.45
Found:	49.05	2.95	23.07	--	4.15	--

Polymeric films were prepared from the polymeric material of Example 4 by casting (onto glass plates) solutions of the polymeric material in a 5 % wt./vol. solution of lithium chloride and dimethylacetamide (5 g lithium chloride per 100 ml of dimethylacetamide). The concentration of polymer was 2 % wt./vol., i.e., 2 g of polymer per 100 ml of the lithium chloride/dimethylacetamide solution. In each instance, the glass plate carrying the puddle-cast polymer solution was immersed in water (after minimal evaporation of solvent). The polymer film was observed to gel and a transparent, colourless unoriented film separated from the glass plate. The resulting film was soaked for 2 days in water to effect extraction of occluded lithium chloride and solvent, soaked in acetone and dried in a vacuum oven at 90°C and 15 mm pressure. Refractive index, measured by interferometry was 1.87.

Stretched polymeric films were prepared in the following manner. Water-ollen films (obtained by soaking the polymer films for several hours for removal of occluded lithium chloride and solvent as aforedescribed) were cut into strips. The strips were

1 mounted between the jaws of a mechanical unidirectional
stretcher. The strips were stretched (in air at 220°C) to
about 50 % elongation, to effect film orientation. The
stretched films were optically transparent. Birefringence,
measured with the aid of a quartz wedge, was 0.24.

5

Solutions of the polymer of Example 4, in a concentration
of 3 to 5 % wt./vol., in lithium chloride-containing
solvents (e.g., dimethylacetamide containing lithium
chloride) were found to form colourless, transparent gels
10 which could be melted and resolidified without thermal
degradation. When the molten solutions were poured into
molds or cast into films, solidification was rapid and the
solid pieces or films were readily removable. The resulting
rubbery solids exhibited high birefringence upon application
15 of very slight stress. Removal of the stress was accompanie
by instantaneous disappearance of the birefringent property

<u>Example 5</u>

20 This example illustrates the preparation of poly(2,2'-di-
bromo-4,4'-biphenylene)-octafluoro-p,p'-biphenylene di-
carboxamide and the preparation therefrom of birefringent
polymeric films.

25 A 50-ml reaction vessel (a resin-making kettle equipped
with a mechanical stirrer, nitrogen inlet tube and calcium
chloride drying tube) was heated while simultaneously
flushing the vessel with nitrogen. After the reaction
vessel had cooled to room temperature, 1.5 g of anhydrous
30 lithium chloride and 0.4571 g (0.001338 mole) of sublimed
2,2'-dibromobenzidine were added while maintaining a
positive nitrogen pressure. The reaction vessel was fitted
with a thermometer and a rubber stopple and 10 ml of an-
hydrous distilled N-methylpyrrolidone (NMP) and 10 ml of
35 anhydrous distilled tetramethylurea (TMU) were carefully

added with the aid of syringes. The resulting mixture was
stirred and warmed to 40°C until all solids had dissolved.
The solution was then cooled in a bath of ice and salt to
a temperature of 0°C. A small amount of lithium chloride
precipitation was observed. Distilled 2,2',3,3',5,5',6,6'-
octafluoro-4,4'-biphenylene dicarbonyl chloride (0.5660 g;
0.001338 mole) was quickly added by means of a funnel to
the stirred, 2,2'-dibromobenzidine solution. An additional
10 ml of TMU (at a temperature of 25°C) were added through
the funnel to the reaction mixture. The temperature of the
reaction mixture did not rise above a temperature of 2°C.
After stirring for 15 minutes, the reaction mixture began
to thicken and streaming birefringence (but not stir
opalescence) was observed. Stirring was continued for an
additional 30 minutes at 4°C and the ice bath was removed.
The temperature of the reaction mixture was observed to
rise to 25°C in 40 minutes at which point the reaction
solution was slightly viscous and cloudy in appearance.
The reaction mixture was warmed gently for 90 minutes with
stirring. The temperature of the reaction mixture rose
during the warming to a maximum temperature of 45°C at
which temperature the reaction solution became homogeneous.
Stirring was continued for 18 hours at 45°C.

The resulting reaction product, a 3 % wt./vol. polymer
solution (3 g of polymer per 100 ml of reaction solvent)
was cooled to 40°C and poured into 200 ml of ice-water in
a blender. The resulting fibrous solid was filtered and
washed (in the blender) twice each with water, acetone and
ether. The product was dried in a vacuum oven at 15 mm
pressure and 90°C for 18 hours. The product, obtained in
87.6 % yield, was a white fibrous polymeric material
having the following recurring structural units:
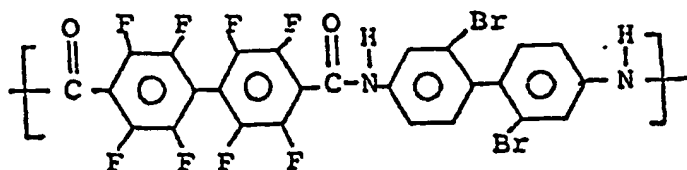
1   The inherent viscosity of a polymer solution (0.5 g of the polymer of Example 5 per 100 ml of a solution of 5 g lithium chloride per 100 ml of dimethylacetamide) was 1.68 dl/g at 30°C.

5   Molecular structure was confirmed by infrared spectroscopy. Inspection of the ultraviolet/visible absorption spectrum for the polymer of Example 5 (in 5 % wt./vol. lithium chloride/dimethylacetamide) showed a λ_{max} of 340 nm and an absorption peak at 360 nm ($\varepsilon = 306$).

10

Elemental analysis for $C_{26}H_8Br_2F_8N_2O_2$ provided the following:

	%C	%H	%Br	%F	%N	%O
Calculated:	45.11	1.17	23.09	21.97	4.05	4.61
Found:	42.89	1.17	21.86	20.81	3.76	9.51 (by difference)

Thermogravimetric analysis showed that onset of degradation of the polymer of Example 5 occurred at 325°C in nitrogen

20 and at 350°C in air. Differential scanning calorimetry showed a reproducible transition at about 155°C.

Polymeric films were prepared from the polymeric material of Example 5 by casting (onto glass plates) solutions of

25 the polymeric material in a 2 % wt./vol. solution of lithium chloride and dimethylacetamide (2 g lithium chloride per 100 ml of dimethylacetamide). The concentration of polymer ranged from 0.5 to 5 % wt./vol., i.e., from 0.5 g to 5 g polymer per 100 ml of the lithium chloride/

30 dimethylacetamide solution. In each instance, the glass plate carrying the puddle-cast polymer solution was immersed in water (after minimal evaporation of solvent). The polymer was observed to gel and a transparent and colourless unoriented film separated from the glass plate.

35 The resulting film was soaked for several hours in water to

effect extraction of occluded lithium chloride and solvent, soaked in acetone and dried in a vacuum oven at 90°C and 15 mm Hg pressure. Refractive index, measured by inter-ferometry was 1.74.

Stretched polymeric films were prepared in the following manner. Water-swollen films (obtained by soaking the poly-mer films for several hours for removal of occluded lithium chloride and solvent as aforedescribed) were cut into strips. The strips were mounted between the jaws of a mechanical unidirectional stretcher. The strips were oriented by stretching (in air at 200°C) to an elongation in the range of 50 to 55 %. The polymeric strips were optically transparent. Birefringence, measured with the aid of a quartz wedge, was 0.35. Strips were also stretched in methanol at 25°C to an elongation of 55 %. Measurement of birefringence for such stretched films showed a bire-fringence of 0.44.
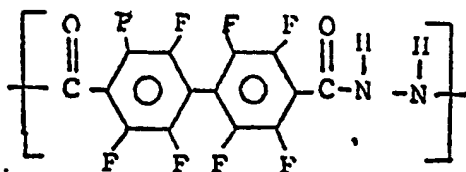
Example 6

This example illustrates the preparation of poly(2,2',3,3', 4,4',6,6'-octafluoro-4,4'-biphenylene) carbohydrazide and the preparation therefrom of birefringent polymeric films.

A 50-ml reaction vessel (a resin-making kettle equipped with a mechanical stirrer, nitrogen inlet tube and calcium chloride drying tube) was heated while simultaneously flushing the vessel with nitrogen. After the reaction vessel had cooled to room temperature, 1.15 g of anhydrous lithium chloride and 0.0386 g (0.001205 mole) of distilled hydrazine were added while maintaining a positive nitrogen pressure. The reaction vessel was fitted with a thermometer and a rubber stopple and 7 ml of anhydrous distilled N-methylpyrrolidone (NMP) and 12 ml of anhydrous distilled tetramethylurea (TMU) were carefully

1 added with the aid of syringes. The resulting mixture was
stirred until most of the lithium chloride had dissolved.
The solution was then cooled in a bath of ice and salt to
a temperature of 0°C. A small amount of lithium chloride
precipitation was observed. Distilled 2,2',3,3',5,5',6,6'-

5 octafluoro-4,4'-biphenylene dicarbonyl chloride (0.5100 g;
0.001205 mole) was quickly added by means of a funnel to the
stirred hydrazine solution. An additional 4 ml of TMU (at a
temperature of 25°C) were added through the funnel to the
reaction mixture. The temperature of the reaction mixture

10 did not rise above a temperature of 5°C. The reaction
mixture did not thicken and streaming birefringence was not
observed. Lithium carbonate (0.0890 g; 0.0024 mole) was
added to the reaction mixture, stirring was continued for
30 minutes at 4°C and the ice bath was removed. As the

15 temperature of the reaction mixture rose to 25°C during
the subsequent 60 minutes, the reaction solution first
became cloudy and, then, a white precipitate formed. Over
the next 30 minutes, the reaction mixture was warmed to
40°C at which time the reaction mixture became homogeneous.

20 The reaction temperature was raised to 70°C and maintained
for 1 hour. No increase in viscosity was apparent.

The reaction product, a 1.99 % wt./vol. polymer solution
(1.99 g of polymer per 100 ml of reaction solvent) was

25 cooled to 40°C and poured into 200 ml of ice-water in a
blender. The resulting powdery solid was filtered and
washed (in the blender) twice each with water, acetone
and ether. The product was dried in a vacuum oven at 15 mm
Hg pressure and 90°C for 18 hours. The polymeric product,

30 obtained in 95.4 % yield, was a white solid material having
the following recurring structural units:

35

1   The inherent viscosity of a polymer solution (0.5 g of the polymer of Example 6 per 100 ml of a solution of 5 g lithium chloride per 100 ml of dimethylacetamide) was 1.16 dl/g at 30°C. The molecular structure of the polymer of Example 6 was confirmed by infrared spectroscopy.

5   Polymeric films were prepared from the polymeric material of Example 6 by casting (onto glass plates) solutions of the polymeric material in a 2 % wt./vol. solution of lithium chloride and dimethylacetamide (2 g lithium

10   chloride per 100 ml of dimethylacetamide). The concentration of polymer ranged from 0.5 to 5 % wt./vol., i.e., from 0.5 g to 5 g polymer per 100 ml of the lithium chloride/ dimethylacetamide solution. In each instance, the glass plate carrying the puddle cast polymer solution was

15   immersed in water (after evaporating the solvent for 1 hour). The polymer film was observed to gel, and a physically weak, cloudy and colourless film separated from the glass plate. The resulting film was soaked for several hours in water to effect extraction of occluded lithium

20   chloride and solvent, soaked in acetone and dried in a vacuum oven at 90°C and 15 mm pressure. The films were not of sufficient strenth to undergo stretching. Refractive index, measured by interferometry, was 1.60.

25

<u>Example 7</u>

This example illustrates the preparation of poly(2,2'-di-bromo-4,4'-biphenylene)-<u>trans</u>-p,p'-stilbene dicarboxamide and the preparation therefrom of birefringent polymeric

30   films.

A 250-ml reaction vessel (a resin-making kettle equipped with a mechanical stirrer, nitrogen inlet tube and calcium chloride drying tube) was heated while simultaneously

35   flushing the vessel with nitrogen. After the reaction

1 vessel had cooled to room temperature, 4.88 g of anhydrous
lithium chloride and 2.1441 g (0.006269 mole) of sublimed
2,2'-dibromobenzidine were added while maintaining a
positive nitrogen pressure. The reaction vessel was fitted
with a thermometer and a rubber stopple and 45 ml of an-
5 hydrous distilled N-methylpyrrolidone (NMP) and 45 ml of
anhydrous distilled tetramethylurea (TMU) were carefully
added with the aid of syringes. The resulting mixture was
stirred and warmed to 40°C until all solids had dissolved.
The solution was then cooled in a bath of ice and salt to
10 a temperature of -5°C. A small amount of lithium chloride
precipitation was observed. Recrystallized trans-p,p'-
stilbene dicarbonyl chloride (1.9129 g; 0.006269 mole) was
quickly added by means of a funnel to the stirred 2,2'-di-
bromobenzidine solution. An additional 30 ml of NMP/TMU
15 mixture (1:1 by weight), at a temperature of 25°C, were
added through the funnel to the reaction mixture. The
temperature of the reaction mixture did not rise above a
temperature of 5°C and then dropped rapidly to -3°C. After
stirring for 30 minutes, the reaction mixture began to
20 thicken and streaming birefringence (but not stir opales-
cence) was observed. Lithium carbonate (0.926 g,
0.01254 mole) was added and stirring was continued for an
additional 30 minutes at 0°C.

25 The ice bath was removed from the reaction vessel, and when
the temperature reached 20°C (in 30 minutes), the reaction
solution had become sufficiently viscous as to begin to
climb the shaft of the mechanical stirrer. A maximum
reaction temperature of 55°C was reached. Stirring was
30 stopped and the mixture was heated overnight at a temper-
ature of 55°C. The reaction product, a viscous polymer
solution of 3 % wt./vol. concentration (3 g of polymer
per 100 ml of reaction solvent) was diluted with 130 ml of
2 % wt./vol. lithium chloride in dimethylacetamide. The
35 resulting polymer solution was poured into 200 ml of ice

and water in a blender. The resulting fibrous solid was filtered and washed (in the blender) twice each with water, acetone and ether. The product was dried in a vacuum oven at 15 mm Hg pressure and 90°C for 18 hours. The polymeric product, obtained in 100 % yield, was a very light-yellow fibrous solid having the following recurring structural units:
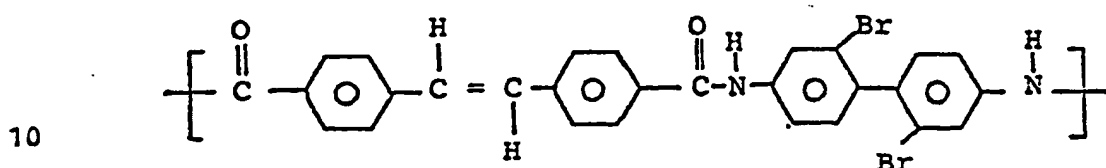
The inherent viscosity of a polymer solution (0.5 g of the polymer of Example 7 per 100 ml of a solution of 5 g lithium chloride per 100 ml of dimethylacetamide) was 9.04 dl/g at 30°C. The molecular weight of the polymer, as determined by light scatterings, was 1.95×10^6, and by gel permeation chromatography, 8.71×10^5.

The molecular structure of the polymer was confirmed by infrared spectroscopy. Inspection of the ultraviolet/ visible spectrum of the polymer (in 5 % wt./vol. lithium chloride/dimethylacetamide) showed a λ_{max} of 352 nm ($\varepsilon = 66,000$); an absorption peak at 368 nm ($\varepsilon = 52,800$) and an extremely weak tail at 400 nm.

Elemental analysis for $C_{28}H_{18}Br_2N_2O_2$ provided the following:

	%C	%H	%Br	%N	%O
Calculated:	58.56	3.16	27.83	4.88	5.57
Found:	58.50	3.22	27.94	4.87	5.47 (by difference)

Thermogravimetric analysis showed that the onset of degradation of the polymer of Example 7 occurred at 470°C

1   in nitrogen and at 515°C in air. Differential scanning
    calorimetry and thermal mechanical analysis of film samples
    detected a reproducible transition at about 225°C.

    Polymeric films were prepared from the polymeric material
5   of Example 7 by casting (onto glass plates) solutions of
    the polymeric material in a 5 % wt./vol. solution of
    lithium chloride and dimethylacetamide (5 g lithium
    chloride per 100 ml of dimethylacetamide). The concentrat-
    ion of polymer ranged from 1 to 5 % wt./vol., i.e., from
10 1 g to 5 g polymer per 100 ml of the lithium chloride/
    dimethylacetamide solution. In each instance, the glass
    plate carrying the puddle-cast polymer solution was
    immersed in water (after minimal evaporation of solvent).
    The polymer was observed to gel and a transparent and
15 colourless unoriented film separated from the soaked glass
    plate. The resulting film was soaked for several hours
    in water to effect extraction of occluded lithium chloride
    and solvent, soaked in acetone and dried in a vacuum oven
    at 90°C and 15 mm Hg pressure. Refractive index, measured
20 by interferometry, was 2.03.

    Stretched polymeric films were prepared in the following
    manner. Water-swollen films (obtained by soaking the poly-
    mer films for several hours for removal of occluded
25 lithium chloride and solvent as aforedescribed) were cut
    into strips. The strips were mounted between the jaws of
    a mechanical unidirectional stretcher. The strips were
    stretched (in air at 220°C) to about 55 to 55 % elongation,
    to effect film orientation. The stretched films were
30 optically transparent. Infrared dichroism indicated that
    the stretched films were less than 65 % by weight oriented;
    the modulus was 0.27×10^6 kg/m^2. Wide-angle X-ray analysis
    of the films showed crystallinity to be less than 10 % by
    weight. Birefringence, measured with the aid of a quartz
35 wedge, was 0.589.

1　Solutions of the polymer of Example 7 in lithium chloride/
dimethylacetamide, as aforedescribed, were formed into
extruded films by the "wet-jet" method whereby the solution
of polymer is extruded into an aqueous coagulation bath for
gelling of the polymer material. The resulting transparent,
5　colourless film strips were soaked in water and cut to
about 25.4 to 50.8 mm for testing. The partially oriented
strips of film produced by the extrusion were further
oriented by stretching in the manner described in the
Examples hereof. Stretching was effected in air at a
10　temperature of 180°C. Elongation was to the break point,
in the range of about 40 % to 50 %. The stretched strips
were optically transparent. Infrared dichroism indicated
that the films were 85 % oriented. Measurement of bire-
fringence utilizing a quartz wedge provided a birefringence
15　value of 0.977. Measurement by resort to interferometry
provided a value of 0.865.

Example 8

20　This example illustrates the preparation of poly(2,2'-di-
bromo-4,4'-biphenylene)-_trans_-α-bromo-biphenylene dicarb-
oxamide and the preparation therefrom of birefringent
polymeric films.

25　A 50-ml reaction vessel (a resin-making kettle equipped
with a mechanical stirrer, a pressure-equalizing dropping
funnel, a nitrogen inlet tube and calcium chloride drying
tube) was heated while simultaneously flushing the vessel
with nitrogen. After the reaction vessel had cooled to
30　room temperature, 1.5 g of anhydrous lithium chloride and
0.4779 g (0.001397 mole) of sublimed 2,2'-dibromo-benzidine
were added while maintaining a positive nitrogen pressure.
The reaction vessel was fitted with a thermometer and a
rubber stopple and 15 ml of anhydrous distilled N-methyl-
35　pyrrolidone (NMP) and 5 ml of anhydrous distilled tetra-

1   methylurea (TMU) were carefully added with the aid of
syringes. The resulting mixture was stirred and warmed to
40°C until all solids had dissolved. The solution was ther
cooled in a bath of ice and salt to a temperature of 0°C.
A small amount of lithium chloride precipitation was ob-

5   served. Recrystallized α-bromo-p,p'-stilbene dicarbonyl
chloride (0.5366 g; 0.001397 mole) was quickly added by
means of a funnel to the stirred 2,2'-dibromobenzidine
solution. An additional 10 ml of TMU (at a temperature of
25°C) were added through the funnel to the reaction mixtur

10   The temperature of the reaction mixture did not rise above
a temperature of 4°C. After stirring for 15 minutes, the
reaction mixture began to thicken and streaming bire-
fringence (but not stir opalescence) was observed. Stirrir
was continued for an additional 30 minutes at 4°C.

15

The ice bath was removed from the reaction vessel and the
temperature was observed to rise to 25°C in 90 minutes at
which point the reaction mixture had become sufficiently
viscous as to climb the shaft of the mechanical stirrer.

20   Over the next 90 minutes, the very pale-yellow reaction
mass was gently warmed with intermittent stirring; the
maximum temperature reached was approximately 70°C.

The reaction product, a 3 % wt./vol. polymer solution

25   (3 g of polymer per 100 ml of reaction solvent) was cooled
to 40°C and poured into 200 ml of ice-water in a blender.
The resulting fibrous solid was filtered and washed (in
the blender) twice each with water, acetone and ether. The
product was dried in a vacuum oven at 15 mm Hg pressure ar

30   90°C for 18 hours. The product, obtained in 95.4 % yield,
was a light-yellow fibrous polymeric material having the
following recurring structural units:

35
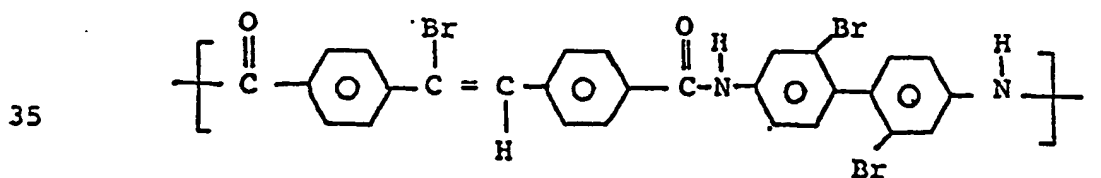
1　The inherent viscosity of a polymer solution (0.5 g of the polymer of Example 8 per 100 ml of a solution of 5 g lithium chloride per 100 ml of dimethylacetamide) was 7.81 dl/g at 30°C.

5　Molecular structure was confirmed by infrared spectroscopy. Elemental analysis for $C_{28}H_{17}N_2Br_3O_2$ provided the following:

	%C	%H	%Br	%N	%O
Calculated:	51.478	2.604	36.724	4.289	4.90
Found:	51.17	2.80	34.82	4.15	7.06 (by difference)

10

Polymeric films were prepared from the polymeric material of Example 8 by casting (onto glass plates) solutions of the polymeric material in a 5 % wt./vol. solution of lithium

15　chloride and dimethylacetamide (5 g lithium chloride per 100 ml of dimethylacetamide). The concentration of polymer ranged from 0.5 to 5 % wt./vol., i.e., from 0.5 g to 5 g polymer per 100 ml of the lithium chloride/dimethylacetamide solution. In each instance, the glass plate carrying the

20　puddle-cast polymer solution was immersed in water (after minimal evaporation of solvent). The polymer was observed to gel and a transparent and colourless unoriented film separated from the soaked glass plate. The resulting film was soaked for several hours in water to effect extraction

25　of occluded lithium chloride and solvent, soaked in acetone and dried in a vacuum oven at 90°C and 15 mm Hg pressure Refractive index, measured by interferometry, was 2.07.

Stretched polymeric films were prepared in the following

30　manner. Water-swollen films (obtained by soaking the polymer films for several hours for removal of occluded lithium chloride and solvent as aforedescribed) were cut into strips. The strips were mounted between the jaws of a mechanical unidirectional stretcher. The strips were

35　stretched (in air at 220°C) to about 60 % to 65 % elongation,

1   to effect film orientation. The stretched strips were
optically transparent. Birefringence, measured with the aid
of a quartz wedge, was 0.680.

Solutions of the polymer of Example 8 in lithium chloride/
5   dimethylacetamide, as aforedescribed, were formed into ex-
truded films by the "wet-jet" method whereby the solution
of polymer is extruded into an aqueous coagulation bath for
gelling of the polymer material. The resulting transparent,
colourless film strips were soaked in water and cut to
10 about 25.4 to 50.8 mm for testing. The partially oriented
strips of film produced by the extrusion were further
oriented by stretching in the manner described in the
Examples hereof. Stretching was effected in air (at a
temperature of 180°C) to the break point, in the range of
15 about 40 % to 50 % elongation. The stretched film strips
were otpically transparent. Measurement of birefringence
utilizing a quartz wedge provided a birefringence value of
0.955. Measurement by resort to interferometry provided a
value of 0.849.
20

Example 9

This example illustrates the preparation of poly(2,2'-di-
bromo-4,4'-biphenylene)-α,α'-dimethylmuconamide and the
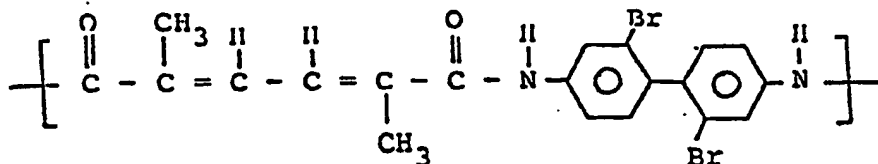25 preparation therefrom of birefringent polymeric films.

A 50-ml reaction vessel (a resin-making kettle equipped with
a mechanical stirrer, a pressure-equalizing dropping funnel,
a nitrogen inlet tube and calcium chloride drying tube) was
30 heated while simultaneously flushing the vessel with nitrogen.
After the reaction vessel had cooled to room temperature,
0.4 g of anhydrous lithium chloride and 0.8519 g (0.00249
mole) of sublimed 2,2'-dibromo-benzidine were added while
maintaining a positive nitrogen pressure. The reaction vessel
35 was fitted with a thermometer and a rubber stopple and 10 ml

of anhydrous distilled N-methylpyrrolidone (NMP) were carefully added with the aid of a syringe. The resulting mixture was stirred and warmed to 40°C until all solids had dissolved. The solution was then cooled in a bath of ice and salt to a temperature of 0°C with formation of some lithium chloride precipitate. A solution of recrystallized α,α'-dimethyl muconyl chloride (0.5157 g; 0.002491 mole) in 6 ml of anhydrous, distilled tetrahydrofuran (THF) was added to the dropping funnel through a rubber stopper with a syringe. The α,α'-dimethyl muconyl chloride/THF solution, the temperature of which was 25°C, was added dropwise over 5 minutes to the cold 2,2'-dibromobenzidine solution while stirring moderately. The addition funnel was rinsed with 6 ml of NMP which was also added dropwise to the reaction mixture in order to prevent the temperature of the reaction mixture from rising above 1°C. After stirring for 1 hour, during which time the solution turned lemon-yellow (but did not thicken), 0.354 g of solid lithium carbonate was added all at once to the reaction mixture. Within 10 minutes noticeable thickening was observed, and after an additional 20 minutes, at 20°C, the viscosity increased further. The ice bath was removed from the reaction vessel and the temperature of the reaction mixture was allowed to rise to 25°C over a one-hour period during which time a thick paste had formed. The temperature of the reaction mixture was increased to 65°C over the next 20 minutes producing a mixture which could no longer be stirred. Additional heating for 18 hours at 55°C without stirring produced a transparent, light-yellow viscous polymer solution. The reaction product, a 5.36 % wt./vol. polymer solution (5.6 g of polymer per 100 ml of reaction solvent) was observed to exhibit considerable streaming birefringence upon application of low mechanical stress; stir opalescence was not, however, observed.

The polymer solution was poured into a blender containing 200 ml of ice-water and the resulting fibrous solid was

1 filtered and washed (in the blender) twice each with water,
acetone and ether. The product was dried in a vacuum oven
at 15 mm Hg pressure and 90°C for 18 hours. The product,
obtained in 94.7 % yield, was a white fibrous polymeric
material having the following recurring structural units:

5

$$\left[\begin{array}{c}\underset{\|}{\overset{O}{C}}-\underset{\underset{CH_3}{|}}{\overset{CH_3}{\underset{|}{C}}}=\overset{\|}{C}-\overset{\|}{C}=\overset{\|}{C}-\overset{O}{\underset{\|}{C}}-\overset{\|}{N}\!\!-\!\!\left\langle\!\!\underset{Br}{\overset{Br}{\bigcirc}}\!\!-\!\!\bigcirc\!\!\right\rangle\!\!-\!\!\overset{\|}{N}\end{array}\right]$$

10 The inherent viscosity of a polymer solution (0.5 g of the
polymer of Example 9 per 100 ml of a solution of 5 g lithium
chloride per 100 ml of dimethylacetamide) was 4.69 dl/g at
30°C.

15 Molecular structure was confirmed by infrared sprectroscopy.
Inspection of the ultraviolet/visible absorption spectrum
for the polymer of Example 9 (in 3 % wt./vol. lithium
chloride/dimethylacetamide showed a λ_{max} of 333 nm (ε =
20 33,600) and an extremely weak tail at 400 nm.

Elemental analysis for $C_{20}H_{16}Br_2N_2O_2$ provided the following:

	%C	%H	%Br	%N	%O
Calculated:	50.448	3.387	33.562	5.883	6.72
Found:	50.09	3.45	34.17	5.72	6.57 (by difference.

Thermogravimetric analysis showed that the onset of
degradation occurred at 360°C in nitrogen and at 310°C in
30 air. Differential scanning calorimetry and thermal mechanic-
al analysis of film samples showed a reproducible transition
at about 185°C.

Polymeric films were prepared from the polymeric material
35 of Example 9 by casting (onto glass plates) solutions of the

1 polymeric material in a 5 % wt./vol. solution of lithium
chloride and dimethylacetamide (5 g lithium chloride per
100 ml of dimethylacetamide). The concentration of polymer
ranged from 2 to 4 % wt./vol., i.e., from 2 g to 4 g polymer
per 100 ml of the lithium chloride/dimethylacetamide solut-
5 ion. In each instance, the glass plate carrying the puddle-
cast polymer solution was immersed in water (after minimal
evaporation of solvent). The polymer film was observed to
gel and a transparent and colourless unoriented film
separated from the glass plate. The resulting film was soaked
10 for several hours in water to effect extracttion of occluded
lithium chloride and solvent, soaked in acetone and dried in
a vacuum oven at 90°C and 15 mm Hg pressure. Refractive
index, measured by interferometry, was 1.91.

15 Stretched polymeric films were prepared in the following
manner. Water-swollen films (obtained by soaking the poly-
mer films for several hours for removal of occluded lithium
chloride and solvent as aforedescribed) were cut into strips.
The strips were mounted between the jaws of a mechanical
20 stretcher and were unidirectionally stretched, successively,
in steam, acetone and boiling ethylne glycol (all of which
function as plasticizers). The strips were stretched to an
elongation of from 35 % to 45 %. The film strips were
further elongated (up to 60%) by stretching in air at 200°C.
25 The stretched strips were optically transparent. Optical
retardation was measured with a calibrated quartz wedge; film
thickness was measured with a micrometer. Birefringence,
measured by means of a quartz wedge, was 0.40.

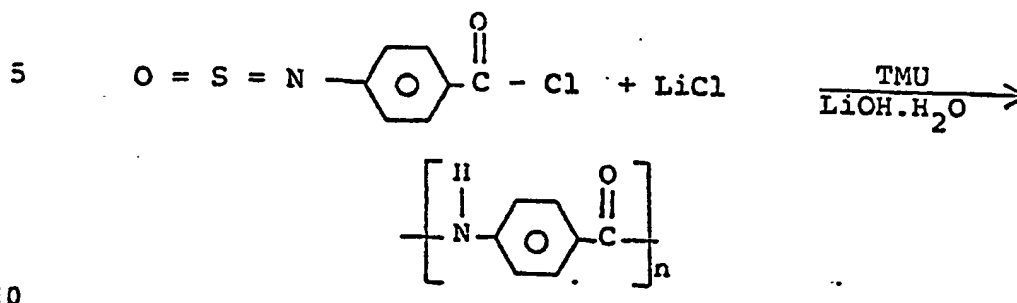Example 10

30

For purposes of comparison with the substituted polyamides
of the present invention, an unsubstituted polyamide was
prepared and evaluated in the following manner.

35

1 A solution polymerization reaction for the production of
poly(p-benzamide) was conducted in accordance with the
following reaction scheme:

5

$$O = S = N -\!\!\!\bigcirc\!\!\!- \overset{\overset{O}{\|}}{C} - Cl \;\; + \; LiCl \quad \xrightarrow[\text{LiOH.H}_2\text{O}]{\text{TMU}}$$

$$\left[\!\!-\overset{\overset{H}{|}}{N}-\!\!\!\bigcirc\!\!\!-\overset{\overset{O}{\|}}{C}\!-\!\!\right]_n$$

10

A 50-ml reaction vessel (a resin-making kettle equipped
with mechanical stirrer, nitrogen inlet tube and calcium
chloride drying tube) was heated while simultaneously

15 flushing the vessel with nitrogen. After the reaction
vessel had cooled to room temperature, 40 ml of anhydrous
distilled tetramethyl urea (TMU), 8.04 g (0.04 mole) of
vacuum-distilled p-thionylaminobenzoyl chloride and 0.52 g
(0.012 mole) of lithium chloride were added while maintain-

20 ing a positive nitrogen pressure. The resulting reaction
mixture was stirred for ten minutes at room temperature and
1.68 g (0.04 mole) of lithium hydroxide monohydrate were
added while vigorously stirring. The reaction mixture was
then stirred for 1 hour at room temperature. After a period

25 of 7 additional minutes, the reaction mixture became cloudy
and was observed to thicken. The polymeric reaction product,
after 20 minutes, thickened sufficiently to adhere the
shaft of the mechanical stirrer. After one-half hours, the
reaction mixture, which could not be stirred, was heated.

30 An additional quantity (14 ml) of TMU was added at which
point the reaction mixture still could not be stirred. The
reaction mixture was then heated to 130°C without stirring.
After 2 hours of heating at 130°C, pliability of polymeric
reaction mass increased and the product appeared to have

35 partially dissolved. The reaction product was stored in the

1 reaction vessel overnight and was washed with water, filter-
ed and washed with acetone then ether. The product, poly-
(p-benzamide) was dried in a vacuum oven at 80°C for
2 hours.

5 The inherent viscosity of a polymer solution of poly(p-
benzamide) in sulfuric acid was 1.60 dl/g at 30°C.

Polymeric films of poly(p-benzamide) were prepared by
casting a solution of the polymeric material in a 5 % wt./
10 vol. solution of lithium chloride and dimethylacetamide
(5 g lithium chloride per 100 ml of dimethylacetamide). The
concentration of polymer was 5 % wt./vol., i.e., 5 g poly-
mer per 100 ml of the lithium chloride/dimethylacetamide
solution. The cast polymer film was dried in a vacuum oven
15 at 90°C overnight. The polymer film was an opaque,
white flexible film. Additional films were formed by
puddle-casting the solution as aforedescribed onto glass
plates. In each instance, the glass plate carrying the
puddle-cast polymer solution was immersed in water (after
20 most of the solvent had evaporated). The polymer film
which separated from the glass plate was a tough, trans-
parent, flexible film. The resulting film was soaked for
several hours in water to effect extraction of occluded
lithium chloride and solvent.

25
Stretched polymeric films were prepared in the following
manner. Water-swollen films (obtained by soaking the poly-
mer films for several hours for removal of occluded
lithium chloride and solvent as aforedescribed) were cut
30 into strips. The strips were mounted between the jaws of
a mechanical stretcher and were unidirectionally stretched,
successively, in steam and in air (at 200°C). The strips
were stretched to an elongation of approximately 10 %. The
resulting streched films were clouded in appearance.
35 Optical retardation was measured with a calibrated quartz

1 wedge; film thickness was measured with a micrometer. Bire-
fringence, measured by means of a quartz wedge, was 0.23.

By inspection of the values of birefringence described in
connection with the substituted polyamides of the present
5 invention and the Examples hereof (Examples 1 to 9), it can
be seen that the birefringence of poly(p-benzamide) of
comparative Example 10, was, in general, decidedly lower.

Example 11

10

This example illustrates the preparation of poly-[2,2'-bis-
(trifluoromethyl)-4,4'-biphenylene]-trans-p,p'-stilbene di-
carboxamide and the preparation therefrom of birefringent
polymeric films.

15

A 100-ml reaction vessel (a resin-making kettle equipped
with a mechanical stirrer, nitrogen inlet tube and calcium
chloride drying tube) was heated while simultaneously flush-
ing the vessel with nitrogen. After the reaction vessel had
20 cooled to room temperature, 1.5 g of anhydrous lithium
chloride and 0.5171 g (0.001615 mole) of recrystallized
2,2'-bis(trifluoromethyl)-benzidine were added while main-
taining a positive nitrogen pressure. The reaction vessel
was fitted with a thermometer and a rubber stopple and 10 ml
25 of anhydrous distilled tetramethylurea (TMU) were carefully
added with the aid of syringes. The resulting mixture was
stirred and warmed to 40°C until all solids had dissolved.
The solution was then cooled in a bath of ice and salt to a
temperature of -5°C. A small amount of lithium chloride
30 precipitation was observed. Recrystallized trans-p,p'-
stilbene dicarbonyl chloride (0.4923 g; 0.001615 mole) was
carefully added by means of a funnel to the stirred 2,2'-
bis(trifluoromethyl)-benzidine solution. An additional 10 ml
of TMU, at a temperature of 0°C, were added through the
35 funnel to the reaction mixture. The temperature of the

1 reaction mixture did not rise above a temperature of 5°C
and then dropped rapidly to -3°C. After stirring for
30 minutes, the reaction mixture began to thicken and
streaming birefringence (but not stir.opalescence) was
observed. Stirring was continued for an additional

5 30 minutes at 0°C.

The ice bath was removed from the reaction vessel, and when
the temperature reached 20°C (in 30 minutes), the reaction
solution had become very viscous. Over the next 75 minutes,

10 the completely colourless, transparent solution was warmed
to 72°C. After. stirring at this temperature for the next
18 hours, the mixture was cooled to 40°C. The resulting
polymer solution was poured into 200 ml of ice and water in
a blender. The resulting fibrous solid was filtered and

15 washed (in the blender) twice each with water, acetone and
ether. The product was dried in a vacuum oven at 15 mm Hg
pressure and 90°C for 18 hours. The polymeric product,
obtained in 99.5 % yield, was a very light-yellow fibrous
solid having the following recurring structural units:

20

25
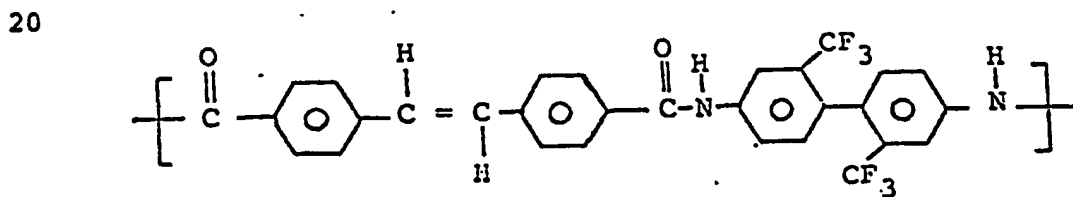
The inherent viscosity of a polymer solution (0.5 g of the
polymer of Example 11 per 100 ml of a solution of 5 g
lithium chloride per 100 ml of dimethylacetamide) was
4.735 dl/g at 30°C. The molecular structure of the polymer

30 was confirmed by infrared spectroscopy.

Elemental analysis for $C_{30}H_{18}F_6N_2O_2$ provided the following:

	%C	%H	%F	%N	%O
Calculated:	65.22	3.28	20.64	5.07	5.79
35 Found:	64.54	3.76	19.04	4.85	7.81 (by difference)

1   Thermogravimetric analysis showed that the onset of de-
gradation of the polymer of Example 11 occurred at 500°C
in nitrogen and at 410°C in air. Differential scanning
calorimetry and thermal mechanical analysis of film samples
detected a reproducible transition at about 185°C.

5   Polymeric films were prepared from the polymeric material
of Example 11 by casting (onto glass plates) solutions of
the polymeric material in a 5 % wt./vol. solution of
lithium chloride and dimethylacetamide (5 g lithium chloride
10 per 100 ml of dimethylacetamide). The concentration of
polymer ranged from 1.0 to 5 % wt./vol., i.e., from 1.0 g
to 5 g polymer per 100 ml of the lithium chloride/dimethyl-
acetamide solution. In each instance, the glass plate
carrying the puddle-cast polymer solution was immersed in
15 water (after minimal evaporation of solvent). The polymer
film was observed to gel and a transparent and colourless
unoriented film separated from the glass plate. The result-
ing film was soaked for several hours in water to effect
extraction of occluded lithium chloride and solvent, soaked
20 in acetone and dried in a vacuum oven at 90°C and 15 mm Hg
pressure. Refractive index, measured by interferometry, was
1.997.

Stretched polymeric films were prepared in the following
25 manner. Water-swollen films (obtained by soaking the poly-
mer films for several hours for removal of occluded
lithium chloride and solvent as aforedescribed) were cut
into strips. The strips were mounted between the jaws of a
mechanical unidirectional stretcher. The strips were
30 stretched (in air at 220°C) to about 60 to 65 % elongation,
to effect film orientation. The stretched films were
optically transparent. Birefringence, measured with the aid
of a quartz wedge, was 0.537.

35 Solutions of the polymer of Example 11 in lithium chloride/

1 dimethylacetamide, as aforedescribed, were formed into
extruded films by the "wet-jet"method whereby the solution
of polymer is extruded into an aqueous coagulation bath
for gelling of the polymer material. The resulting tans-
parent, colourless film strips were soaked in water and
5 cut to about 25.4 to 50.8 mm for testing. The partially
oriented strips of film produced by the extrusion were
further oriented by stretching in the manner described in
the Examples hereof. Stretching was effected to an elong-
ation of less than 20 %. The stretched strips were.
10 optically transparent. Infrared dichroism indicated that
the films were 92 % oriented. Measurement of birefringence
utilizing a quartz wedge provided a birefringence value of
0.879.

15

Example 12

This example illustrates the preparation of poly-[2,2'-bis-
(trifluoromethyl)-4,4'-biphenylene]-2,2'-dimethoxy-4,4'-bi-
phenyl and the preparation therefrom of birefringent poly-
20 meric films.

A 100-ml reaction vessel (a resin-making kettle equipped
with a mechanical stirrer, a pressure-equalizing dropping
funnel, a nitrogen inlet tube and calcium chloride drying
25 tube) was heated while simultaneously flushing the vessel
with nitrogen. After the reaction vessel had cooled to room
temperature, 3.0 g of anhydrous lithium chloride and
0.4328 g (0.001352 mole) of recrystallized 2,2'-bis(tri-
fluoromethyl)benzidine were added while maintaining a
30 positive nitrogen pressure. The reaction vessel was fitted
with a thermometer and a rubber stopple and 20 ml of an-
hydrous distilled N-methylpyrrolidinone (NMP) and 20 ml of
anhydrous distilled tetramethylurea (TMU) were carefully
added with the aid of syringes. The resulting mixture was
35 stirred and warmed to 40°C until all solids had dissolved.

1   The solution was then cooled in a bath of ice and salt to a
temperature of -5°C. A small amount of lithium chloride
precipitation was observed. Recrystallized 2,2'-dimethoxy-
4,4'-biphenyldicarbonyl chloride (0.4586 g; 0.001352 mole)
was quickly added by means of a funnel to the stirred
5   2,2'-bis(trifluoromethyl)-benzidine solution. An additional
20 ml of TMU (at a temperature of 0°C) were added through
the funnel to the reaction mixture. The temperature of the
reaction mixture did not rise above a temperature of 5°C.
After stirring for 30 minutes, the reaction mixture began
10   to thicken and turned milk-like in appearance. Stirring was
continued for an additional 30 minutes at 0°C.

The ice bath was removed from the reaction vessel and the
temperature was observed to rise to 20°C in 30 minutes at
15   which point the reaction mixture was viscous and opaque.
Over the next 75 minutes, the opaque reaction mass was
gently warmed to 40°C at which point it became transparent.
After stirring at this temperature for the next 18 hours,
the reaction mixture was cooled to 30°C and poured into
20   400 ml of ice-water in a blender. The resulting fibrous
solid was filtered and washed (in the blender) twice each
with water and ether. The product was dried in a vacuum oven
at 15 mm Hg pressure and 90°C for 18 hours. The product,
obtained in 99.3 % yield, was an off-white fibrous polymeric
25   material exhibiting solubility in acetone or tetrahydro-
furan and having the following recurring structural units:
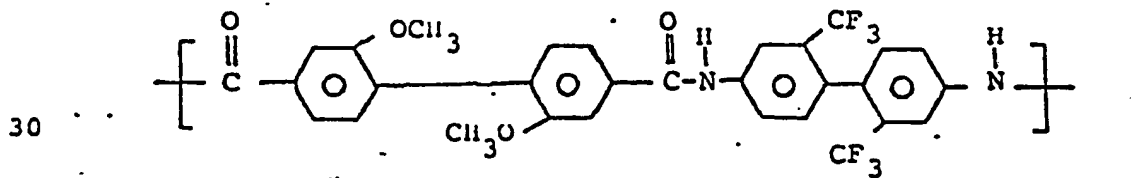
The inherent viscosity of a polymer solution (0.5 g of the
polymer of Example 12 per 100 ml of a solution of 5 g
35   lithium chloride per 100 ml of dimethylacetamide) was
1.69 dl/g at 30°C.

1 Molecular structure was confirmed by infrared spectroscopy.
Inspection of the ultraviolet visible spectrum of the poly-
mer (in 5 % wt./vol. lithium chloride/dimethylformamide)
showed a λ_{max} of 316 nm ($\mathcal{E}$ = 2.59 x 10^3).

5 Elemental analysis for $C_{30}H_{20}F_6N_2O_4$ provided the following:

	%C	%H	%F	%N	%O
Calculated:	61.34	3.43	19.41	4.77	10.89
Found:	59.82	3.51	18.70	4.62	13.35 (by difference)

10 Thermogravimetric analysis showed that the onset of de-
gradation of the polymer of Example 12 occurred at 470°C
in nitrogen and at 440°C in air. Differential scanning
colorimetry detected a reproducible transition at about
15 180°C.

Polymeric films were prepared from the polymeric material of
Example 12 by casting (onto glass plates) solutions of the
polymeric material in a 5 % wt./vol. solution of lithium
20 chloride and dimethylacetamide (5g lithium chloride per
100 ml of dimethylacetamide). The concentration of polymer
ranged from 1 % to 5 % wt./vol., i.e., from 1.0 g to 5 g
polymer per 100 ml of the lithium chloride/dimethylacetamide
solution. In each instance, the glass plate carrying the
25 puddle-cast polymer solution was immersed in water (after
minimal evaporation of solvent). The polymer was observed
to gel and a transparent and colourless unoriented film
separated from the soaked glass plate. The resulting film
was soaked for several hours in water to effect extraction
30 of occluded lithium chloride and solvent, soaked in acetone
and dried in a vacuum oven at 90°C and 15 mm Hg pressure.
Refractive index, measured by interferometry, was 1.73.

Solutions of the polymer of Example 12 in lithium chloride/
35 dimethylacetamide, as aforedescribed, were formed into

1   extruded films by the "wet-jet" method whereby the solution
of polymer is extruded into an aqueous coagulation bath for
gelling of the polymer material. The resulting transparent,
colourless film strips were soaked in water and cut to
about 25.4 to 50.8 mm for testing. The partially oriented
5   strips of film produced by the extrusion were further
oriented by stretching in the manner described in the
Examples hereof. Stretching was effected in air (at a
temperature of 180°C) to an elongation of less than 20 %.
The stretched film strips were otpically transparent. Infra-
10   red dichroism indicated that the films were 92 % oriented.
Measurement of birefringence utilizing a quartz wedge pro-
vided a birefringence value of 0.586.

Example 13

15

  This example illustrates the preparation of poly[2,2',3",-
2"'-tetrakis(trifluoromethyl)-1,1':4',1":4",1"':4'"-
quaterphenylene]-trans-p,p'-stilbenedicarboxamide and the
preparation therefrom of birefringent polymeric films.

20

  A100-ml reaction vessel (a resin-making kettle equipped
with a mechanical stirrer, nitrogen inlet tube and calcium
chloride drying rube) was heated while simultaneously
flushing the vessel with nitrogen. After the reaction vessel
25   had cooled to room temperature, 1.5 g of anhydrous lithium
chloride and 0.5806 g (0.0009543 mole) of recrystallized
4,4"'-diamino-2,2',3",2"'-tetrakis(trifluoromethyl)1,1':4'-
1":4",1"'-quaterphenyl were added while maintaining a
positive nitrogen pressure. The reaction vessel was fitted
30   with a thermometer and a rubber stopple and 10 ml of an-
hydrous distilled N-methylpyrrolidone (NMP) and 10 ml of
anhydrous distilled tetramethylurea (TMU) were carefully
added with the aid of syringes. The resulting mixture was
stirred and warmed to 40°C until all solids had dissolved.
35   The solution was then cooled in a bath of ice and salt to a

1 temperature of -5°C. A small amount of lithium chloride
precipitation was observed. Recrystallized _trans_-p,p'-
stilbene dicarbonyl chloride (0.2909 g; 0.0009543 mole) was
carefully added by means of a funnel to the stirred diamino-
quaterphenyl solution. An additional 10 ml of TMU, at a
5 temperature of 0°C, were added through the funnel to the
reaction mixture. The temperature of the reaction mixture
did not rise above a temperature of 7°C and then dropped
rapidly to 0°C. After stirring for 30 minutes, the reaction
mixture began to thicken and streaming birefringence (but
10 not stir opalescence) was observed. Stirring was continued
for an additonal 30 minutes 0°C.

The ice bath was removed from the reaction vessel, and when
the temperature reached 20°C (in 30 minutes), the reaction
solution had become very viscous. Over the next 75 minutes,
15 the light yellow, opaque solution was warmed to 45°C. After
stirring at this temperature for the next 18 hours, the
transparent polymer solution was poured into 200 ml of ice
and water in a blender. The resulting fibrous solid was
20 filtered and washed (in the blender) twice each with water
and ether. The product was dried in a vacuum oven at 15 mm
Hg pressure and 90°C for 18 hours. The polymeric product,
obtained in 92.2 % yield, was a very light-yellow fibrous
solid having the following recurring structural units:

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25
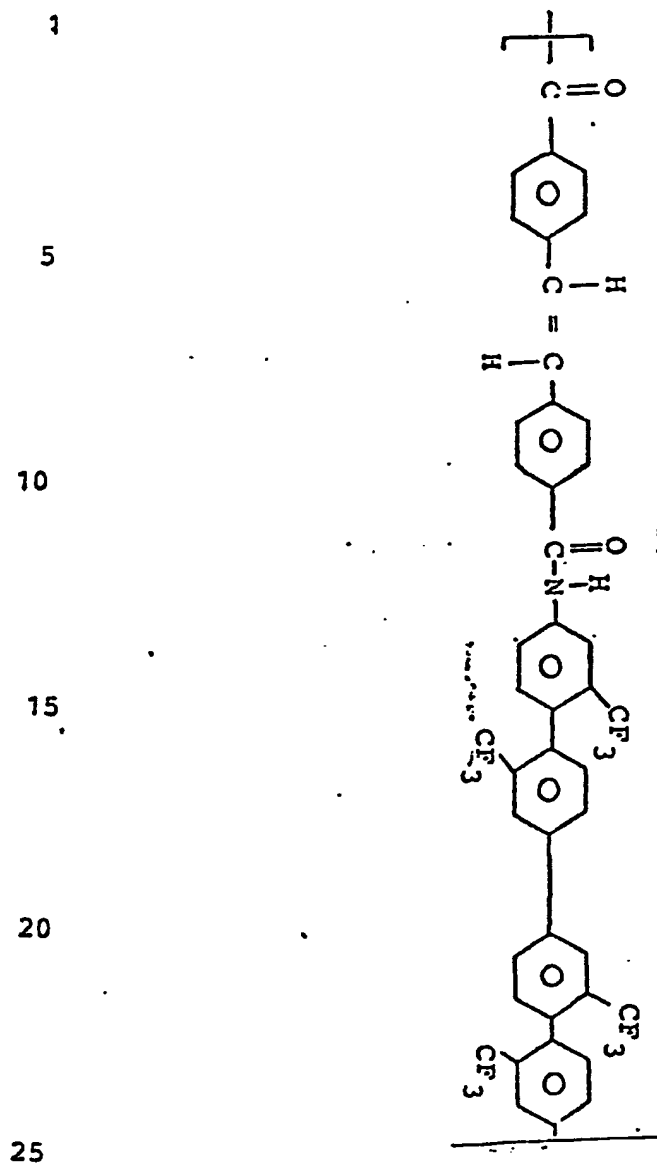
The inherent viscosity of a polymer solution (0.5 g of the
polymer of Example 13 per 100 ml of a solution of 5 g
lithium chloride per 100 ml of dimethylacetamide) was
1.31 dl/g at 30°C. The molecular structure of the polymer
was confirmed by infrared spectroscopy. The polymer was
soluble in tetrahydrofuran, in acetone and in various
amide-type solvent, with and without added lithium
chloride.

30

Elemental analysis for $C_{44}H_{24}F_{12}N_2O_2$ provided the following:

35

	%C	%H	%F	%N	%O
Calculated:	62.86	2.88	27.12	3.33	3.81
Found:	62.07	3.29	24.18	3.16	7.3

(by difference)

Thermogravimetric analysis showed that the onset of degradation of the polymer of Example 13 occurred at 510°C in nitrogen and at 440°C in air. Differential scanning calorimetry and thermal mechanical analysis of film samples detected a reproducible transition at about 187°C.

Polymeric films were prepared from the polymeric material of Example 13 by casting (onto glass plates) solutions of the polymeric material in a 5 % wt./vol. solution of lithium chloride and dimethylacetamide (5 g lithium chloride per 100 ml of dimethylacetamide). The concentration of polymer ranged from 0.5 to 5 % wt./vol., i.e., from 0.5 g to 5 g polymer per 100 ml of the lithium chloride/dimethylacetamide solution. In each instance, the glass plate carrying the puddle-cast polymer solution was immersed in water (after minimal evaporation of solvent). The polymer film was observed to gel and a transparent and colourless unoriented film separated from the glass plate. The resulting film was soaked for several hours in water to effect extraction of occluded lithium chloride and solvent, soaked in acetone and dried in a vacuum oven at 90°C and 15 mm Hg pressure. Refractive index, measured by interferometry, was 1.810.

Stretched polymeric films were prepared in the following manner. Water-swollen films (obtained by soaking the polymer films for several hours for removal of occluded lithium chloride and solvent as aforedescribed) were cut into strips. The strips were mounted between the jaws of a mechanical unidirectional stretcher. The strips were stretched in methanol and then in air at 220°C to effect film orientation. The stretched films were optically transparent. Bire-

1 fringence, measured with the aid of a quartz wedge, was
0.87.

Example 14

5 This example illustrates the preparation of poly-[2,2',3",
2"'-tetrakis(trifluoromethyl)-1,1':4', 1":4", 1"'-4"'-
quaterphenylene] terephthalamide and the preparation there-
from of birefringent polymeric films.

10 A 100 ml reaction vessel (a resin-making kettle equipped
with a mechanical stirrer) nitrogen inlet tube and calcium
chloride drying tube) was heated while simultaneously
flushing the vessel with nitrogen. After the reaction
vessel had cooled to room temperature, 1.5 g of anhydrous
15 lithium chloride and 0.6301 g (0.001036 mole) of recrystall-
ized 4,4"'-diamino-2,2',3",2"'-tetrakis(trifluoromethyl)-
1,1':4',1";4",1"'-quaterphenyl were added while maintaining
a positive nitrogen pressure. The reaction vessel was fitted
with a thermometer and a rubber stopple and 10 ml of an-
20 hydrous distilled N-methylpyrrolidone (NMP) and 10 ml of
anhydrous distilled tetramethylurea (TMU) were carefully
added with the aid of syringes. The resulting mixture was
stirred and warmed to 40°C until all solids had dissolved.
The solution was then cooled in a bath of ice and salt to a
25 temperature of +5°C. A small amount of lithium chloride
precipitation was observed. Recrystallized terephthaloyl-
chloride (0.2103 g; 0.001036 mole) was carefully added by
means of a funnel to the stirred 2,2'-diaminoquaterphenyl
solution. An additional 10 ml of TMU, at a temperature of
30 10°C, were added through the funnel to the reaction mixture.
The temperature of the reaction mixture did not rise above
a temperature of 15°C and then dropped to 10°C. After
stirring for 30 minutes, the reaction mixutre began to
thicken and streaming birefringence (but not stir
35 opalescence) was observed. Stirring was continued for an
additional 30 minutes at 10°C.

1 The ice bath was removed from the reaction vessel, and when the temperature reached 27°C (in 30 minutes), the reaction solution had become very viscous. Over the next 75 minutes, the light yellow, transparent solution was warmed to 40°C. After stirring at this temperature for the next 18 hours,

5 the polymer solution was poured into 200 ml of ice and water in a blender. The resulting fibrous solid was filtered and washed (in the blender) twice each with water and ether. The product was dried in a vacuum oven at 15 mm Hg pressure and 90°C for 18 hours. The polymeric product, obtained in

10 93.5 % yield, was a white fibrous solid having the following recurring structural units:
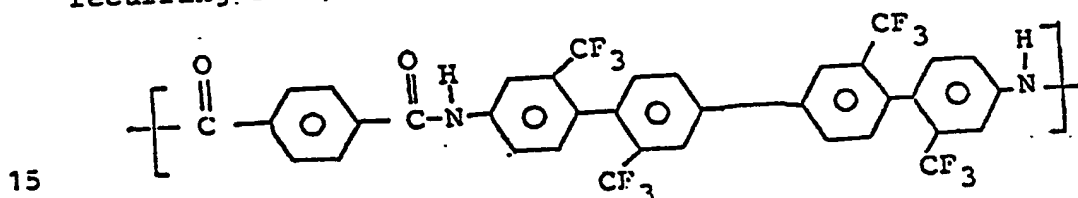
The inherent viscosity of a polymer solution (0.5 g of the polymer of Example 14 per 100 ml of a solution of 5 g

20 lithium chloride per 100 ml of dimethylacetamide) was 6.55 dl/g at 30°C. The molecular structure of the polymer was confirmed by infrared spectroscopy. The polymer was very slightly soluble in acetone, in tetrahydrofuran and in ethyl acetate and was soluble in amide-type solvents with

25 or without added lithium chloride.

Elemental analysis for $C_{36}H_{18}F_{12}N_2O_2$ provided the following:

	%C	%H	%F	%N	%O
Calculated:	58.23	2.44	30.71	3.77	4.85
Found:	57.87	2.50	30.56	3.77	5.3 (by difference)

30

Thermogravimetric analysis showed that the onset of degradation of the polymer of Example 14 occurred at 440°C in

35 nitrogen and in air. Differential scanning calorimetry and

1   thermal mechanical analysis of film samples detected a
reproducible transition at about 160°C.

Polymeric films were prepared from the polymeric material
of Example 13 by casting (onto glass plates) solutions of
5   the polymeric material in a 5 % wt./vol. solution of
lithium chloride and dimethylacetamide (5 g lithium
chloride per 100 ml of dimethylacetamide). The concentrat-
ion of polymer ranged from 0.5 to 5 % wt./vol., i.e. from
0.5 g to 5 g polymer per 100 ml of the lithium chloride/di-
10 methylacetamide solution. In each instance, the glass plate
carrying the puddle-cast polymer solution was immersed in
water (after minimal evaporation of solvent). The polymer
film was observed to gel and a transparent and colourless
unoriented film separated from the glass plate. The result-
15 ing film was soaked for several hours in water to effect
extraction of occluded lithium chloride and solvent, soaked
in acetone and dried in a vacuum oven at 90°C and 15 mm Hg
pressure. Refractive index, measured by interferometry,
was 1.79.

20
Stretched polymeric films were prepared in the following
manner. Water-swollen films (obtained by soaking the poly-
mer films for several hours for removal of occluded lithium
chloride and solvent as aforedescribed) were cut into
25 strips. The strips were mounted between the jaws of a
mechanical unidirectional stretcher. The strips were
stretched (in air at 220°C) to effect film orientation. The
stretched films were optically transparent. Birefringence,
measured with the aid of a quartz wedge, was 0.293.

30
Solutions of the polymer of Example 14 in lithium chloride/
dimethylacetamide, as aforedescribed, were formed into
extruded films by the "wet-jet" method whereby the solution
of polymer is extruded into an aqueous coagulation bath for
35 gelling of the polymer material. The resulting transparent

colourless film strips were soaked in water and cut to
about 25.4 to 50.8 mm for testing. The partially oriented
strips of film produced by the extrusion were further
oriented by stretching in the manner described in the
Examples hereof. Measurement of birefringence itilizing a
quartz wedge provided a birefringence value of 0.44.

Example 15

Geometric indices were determined for the repeating units of
polymeric materials having the following structure
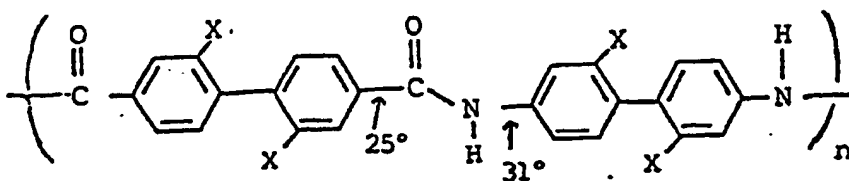
wherein each X is hydrogen or a substituent as set forth in
the following Table I. In the case of each recurring unit,
the eccentricity factor $\dfrac{1 + e_L}{1 + e_T}$ was calculated and is report-
ed in Table I. Bond and group polarizability tensors were
utilized to calculate a polarizability matrix for each
repeat unit, the diagonalized form of the matrix providing
the X, Y and Z contributions to the unit polarizability
ellipsoid. Axial polarizablilities; i.e., X, Y and Z, were
utilized to calculate longitudinal and transverse
eccentricities of each repeat unit, thus, reflecting its
symmetry.

Eccentricity values were calculated utilizing the following
procedure. A polarizability and a corresponding orthogonal
coordinate system is assigned to each segment of the poly-
mer repeat unit. Literature values for group polarizabil-
ities are utilized from the literature, or where not avail-
able, are constructed from bond polarizabilities. Available
Denbigh values were utilized herein for all calculations.

1   Bond polarizabilities are utilized to connect segments where necessary. To determine the overall polarizability of the repeat unit, the coordinate system of the segment at one end of the repeat unit os made coincident with that of the adjacent segment by means of the appropriate rotat-

5   ion(s). This procedure is repeated on each successive segment until the last segment is reached. Mathematically, this means that the matrix of one segment must be pre- and post-multiplied by a transformation matrix:

10

$$\alpha_1' = \underline{T} \; \alpha_1 \cdot T^{-1}$$

where α_1 is the polarizability of segment 1; $\underline{T}$ is the transformation matrix; T^{-1} is the inverse of $\underline{T}$; and α_1' is the polarizability of segment 1 in the coordinate system of

15   segment 2. The value of α_1' is then added to α_2 and the transformation repeated. The repeat unit polarizability matrix is diagonalized, thus, providing a repeat unit polarizability ellipsoid with three semi-axes, i.e., α_{xx}, α_{yy}, and α_{zz}, where α_{xx} is the major polarizability and

20   is coincident with the polymer backbone.

Literature-reported values of 25° and 31°, respectively, were utilized in all calculations as representing the di- hedral angle betweeen the phenyl and carbonyl moieties and

25   the dihedral angle between the phenyl and amino moieties, respectively, Experimentally determined values for the di- hedral angle between each X-substituted phenyl moiety were utilized in all calculations and are reported in Table I. Mean diameter values, D, and length, L, were obtained from

30   spacefilling molecular models.

35

TABLE I

Substituent X (Dihedral Angle)	Mean Diameter (D)	Length (L)	$\left(\dfrac{1 + e_L}{1 + e_T}\right)$	G
H (20°)	4.49	21.35	1.061	0.989
F (60°)	4.61	21.35	1.206	1.21
Cl (72°)	4.78	21.35	1.348	1.23
Br (75°)	4.83	21.35	1.388	1.24
I (85°)	4.91	21.35	1.428	1.26
CF_3 (80°)	4.90	21.35	1.496	1.33
CH_3 (71°)	4.76	21.35	1.330	1.25

From the data presented in Table I will be observed the influence of the nature of the X substituent relative to a hydrogen atom as regards the reported dihedral angle and resulting substantial noncoplanarity between interbonded phenyl rings. Differences in mean diameter and influence of the nature of X substituents on mean diameter and eccentricity factor, and correspondingly, geometric index G will also be observed. Thus, it will be noted that the largest substituents, i.e., $-CF_3$ and $-I$ substituents, corresponded with the largest dihedral angles between interbonded phenyl groups or the hightest non-coplanarity and, accordingly, recurring units having such substituents show high geometric index values.

For purposes of comparison, geometric index G was calculated for the repeat unit of poly(p-phenylene)terephthalamide having the following structure and the results thereof are

reported in Table II. Dihedral ange values of 25° and 31° were utilized for purposes of calculation as in the case of the repeat units of Example 15.
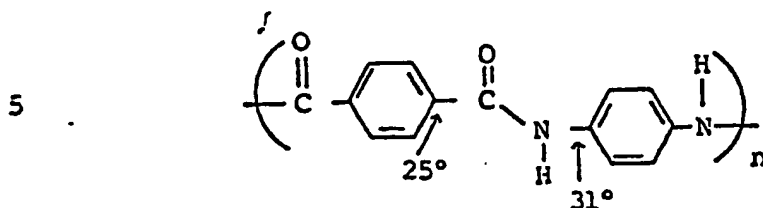
TABLE II

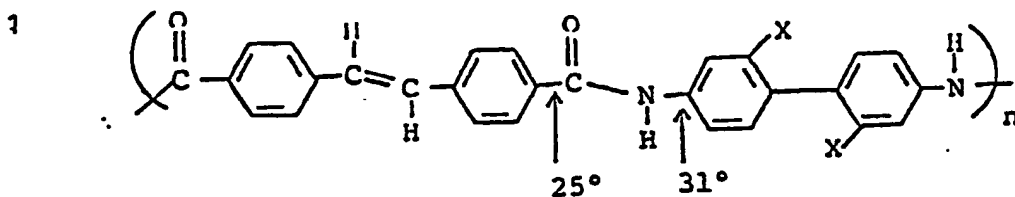| Mean Diameter (D)	Length (L)	$\dfrac{1 + e_L}{1 + e_T}$	G
4.43	12.45	0.978	0.621

As can be observed from inspection of the data reported in Tables I and II, the geometric indices for the repeat units og zhr materials set forth in Table I are considerably higher than the geometric index calculated for poly(p-phenylene)therephthalamide of Table II.

Example 16

Geometric indices for the recurring units of polyamides having the following structure were calculated. Each X substituent was as indicated in Tabele III. Dihedral angles from the literature were utilized in such calculations. Calculated geometric indices were compared with values of theoretical maximum birefringence for the polymeric materials, reported in Table III. Theoretical maximum birefringence values (Δn_{max}) were obtained by plotting the orientation function, calculated from infrared dichroism, against experimental birefringence and extrapolating to 100 % orientation. The results are set forth in Table III.

1

$$\left(\begin{array}{c} O \\ \parallel \\ C \end{array} - \hspace{-4pt}\left\langle \right\rangle\hspace{-4pt} - \begin{array}{c} H \\ \parallel \\ C \end{array}\hspace{-2pt}=\hspace{-2pt}\begin{array}{c} \\ C \\ \mid \\ H \end{array} - \hspace{-4pt}\left\langle \right\rangle\hspace{-4pt} - \begin{array}{c} O \\ \parallel \\ C \end{array} - N - \hspace{-4pt}\underset{X}{\left\langle \right\rangle}\hspace{-4pt} - \hspace{-4pt}\underset{X}{\left\langle \right\rangle}\hspace{-4pt} - \begin{array}{c} H \\ \mid \\ N \end{array}\right)_n$$

25°   31°

5

TABLE III

Substituent X (Dihedral Angle)	G	Δn_{max}
-Br (75°)	1.21	1.20
-CF$_3$ (80°)	1.18	0.98

15 From the data presented in Table III, it will be seen that high values of geometric index G corresponded with high values of Δn_{max}. For purposes of comparison, the theoretical maximum birefringence value (Δn_{max}) for the recurring unit of poly(p-phenylene)terephthalamide (having a G value of

20 0.621 as shown in Table II) was also determined. The resulting Δn_{max} value of 0.83 for poly(p-phenylene)terephthalamide was higher than would be predicted from the geometric index value, G, of 0.621. This is believed to be the result of the highly crystalline nature of the poly(p-phenylene)tereph-

25 thalamide material, whereas the geometric index G reflects the inherent anisotropy of an isolated chain independent of such macroscopic properties as morphology, density, colour or the like.

30 The enhanced optical anisotropy exhibited by the preferred substituted-aromatic polyamide materials utilized in the optical devices hereof is believed to be the result of the rigid, rod-like uniaxial molecular structure of such materials and the amorphous/crystalline ratio thereof.

35 This ratio typically ranges from about 10:1 to about 20:1.

In the case of highly unidirectionally oriented phenyl-type
polyamides this ratio generally will be in the range of
about 0.3:1. The presence of crystallites is generally
detrimental in polymeric materials adapted to utilization
in optical devices owing to light scattering and diminished
transparency. The non-coplanarity between substituted bi-
phenyl rings, resulting from sterically bulky groups on
the ortho positions of interbonded phenyl rings, raises the
amorphous/crystalline ratio to a range of about 10:1 to
about 20:1. This permits the fabrication of highly oriented
films and fibres exhibiting high transparency in addition
to high birefringence. The ring-substituted biphenyl poly-
amides additionally exhibit enhanced solubility and can be
fabricated into colourless films or fibres where desired.

Example 17

Geometric indices were determined for the repeating units
of polymeric materials having the following structure
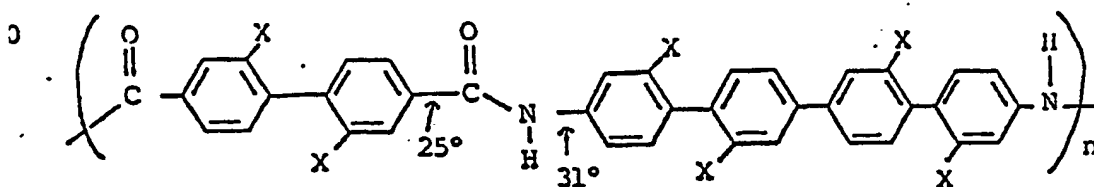
wherein each X is hydrogen or a substituent as set forth in
the following Table IV. In the case of each recurring unit,

the eccentricity factor $\dfrac{1 + e_L}{1 + e_T}$ was calculated and is

reported in Table IV. Bond and group polarizability matrix
for each repeat unit, the diagonalized form of the matrix
providing the X, Y and Z contributions to the unit
polarizability ellipsoid. Axial polarizabilities, i.e., X,
Y and Z, were utilized to calculate longitudinal and trans-
verse eccentricities of each repeat unit, thus, reflecting
its symmetry.

1   Eccentricity values were calculated utilizing the procedure
set forth in Example 15.

Literature-reported values of 25° and 31°, respectively,
were utilized in all calculations as representing the di-
5   hedral angle between the phenyl and carbonyl moieties and
the dihedral angle between the phenyl and amino moieties,
respectively. Experimentally determined values for the di-
hedral angle between each X-substituted phenyl moiety were
utilized in all calculations and are reported in Table IV.
10 Mean diameter values, D, and length, L, were obtained from
space-filling molecular models.

Table IV

Substituent X (Dihedral Angle)	Mean Diameter (D)	Length (L)	$\left(\dfrac{1 + e_L}{1 + e_T}\right)$	G
H (20°)	4.52	29.80	0.938	1.373
F (60°)	4.66	29.80	1.155	1.640
Cl (72°)	4.84	29.80	1.166	1.594
Br (75°)	4.90	29.80	1.145	1.546
I (85°)	4.99	29.80	1.271	1.685
CF_3 (80°)	4.98	29.80	1.286	1.708
CH_3 (71°)	4.82	29.80	1.181	1.621

From the data presented in Table IV will be observed the
influence of the nature of the X substituent relative to a
hydrogen atom as regards the reported dihedral angle and
35 resulting substantial noncoplanarity between interbonded

1   phenyl rings. Differences in mean diameter and influence of
    the nature of X substituents on mean diameter and
    eccentricity factor, and correspondingly, geometric index G
    will also be observed. Thus, it will be noted that the
    largest substituents, i.e., $-CF_3$ and $-I$ substituents,
5   corresponded with the largest dihedral angles between
    interbonded phenyl groups or the highest non-coplanarity
    and, accordingly, recurring units having such substituents
    show high geometric index values.

10   · Example 18

    A light-polarizing device utilizing a highly birefringent
    polyamide material was constructed in the following manner.

15 A sheet of birefringent material was prepared from the
    polyamide of Example 11, i.e., poly[2,2'-bis(trifluoro-
    methyl)-4,4'-biphenylene]-trans-p,p'-stilbene dicarboxamide.
    The sheet was prepared by the "wet-jet" extrusion method
    described in Example 11. The resulting extruded polymer, in
20 the form of a partially oriented transparent colourless
    film, was soaked in water and cut into strips. The strips
    were then further oriented by stretching in air in the manner
    also described in Example 11. A strip of the birefringent
    polymer (having perpendicular and parallel indices of
25 refraction, respectively, of approximately 1.72 and 2.34
    and an approximate thickness of 25μm) was embossed by con-
    tacting one surface of the strip with a brass prismatic
    plate heated to a temperature of 180°C. and pressing the
    heated plate onto the surface of the film so as to provide
30 a prismatic layer of birefringent material generally shown
    in Fig. 6 as layer 42.

    Onto a sheet of transparent isotropic glass material of
    approximately 1-mm thickness was poured a layer of poly-
35 chlorinated biphenyl, an isotropic material having an index

1   of refraction of 1.654, available as Aroclor 1260 ® from
Monsanto Company, St. Louis, Missouri. The prismatic layer
of birefringent material, prepared as aforesaid, was
placed onto the layer of Aroclor. The prismatic layer was
covered with a second layer of Aroclor so as to embed the

5   prismatic layer in Aroclor material. A second sheet of
glass was placed onto the Aroclor so as to sandwich the
birefringent and Aroclor materials between the two pieces
of glass. The resulting polarizer device was tested for
its light polarizing properties by placing the test device

10   and a second polarizer into the path of a light beam and by
observing the attenuation of light resulting from rotation
of the respective polarizers.

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Claims

1. An optical device including a transparent molecularly
oriented highly birefringent polymer, said highly bire-
fringent polymer comprising repeating molecular units ex-
5   hibiting high electron density substantially cylindrically
distributed about the long axes of the polymer and the
repeating units thereof, said highly birefringent polymer
being substantially optically uniaxial exhibiting only two
indices of refraction.
10

2. A device according to claim 1 wherein the birefringence
of said polymer is in relation to the molecular configur-
ation of said repeating molecular units and the cylindrical
or ellipsoidal electron density distribution about said
15 exes according to a dimensionless geometric index G re-
presented by the relationship

$$G = 0.222 \times E \times \frac{L}{D}$$

20 wherein E is a dimensionless eccentricity factor defined by
the relationship

$$E = \frac{1 + e_L}{1 + e_T}$$

25
where e_L is the longitudinal eccentricity of the electron
polarizability of the repeating molecular unit and e_T is
the transverse eccentricity of the polarizability of the
repeating molecular unit, L is the length of the repeating
30 molecular unit along the main axis thereof and D is the
mean diameter of the repeating molecular unit and wherein
said geometric index G has a value of about 0.5 or higher.

3. A device according to claim 2 wherein said geometric
35 index G has a value of at least one, preferably at
least 1.2.

1   4. A device according to any preceding claim wherein said molecularly oriented highly birefringent polymer has a birefringence of at least 0.2, preferably at least 0.4.

5   5. A device according to any preceding claim wherein said molecularly oriented highly birefringent polymer is in the form of a unidirectionally stretched polymer layer.

     6. A device according to claim 1 wherein said molecularly oriented highly birefringent polymer comprises recurring
10   units of the formula

$$\left[\overset{O}{\underset{\parallel}{C}} - A \left(\overset{O}{\underset{\parallel}{C}} - \overset{R}{\underset{N}{}} - B\right)_c \overset{R^1}{\underset{N}{}}\right] \quad ,$$
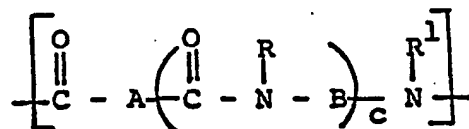
15   wherein each of A and B is a divalent radical except that B can additionally represent a single bond; R and R^1 are each hydrogen, alkyl, aryl, alkaryl or aralkyl; and c is zero or one; and wherein, when c is one, at least one of
20   A and B is a divalent radical selected from the group consisting of:
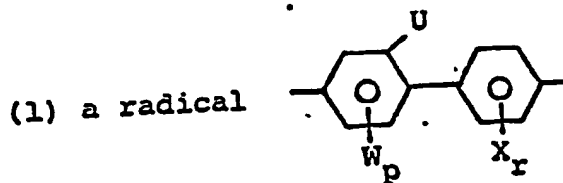
     (1) a radical

     where U is a substituent other than hydrogen, each W is hydrogen or a substituent other than hydrogen, p is an
30   integer from 1 to 3, X is hydrogen or a substituent other than hydrogen and r is an integer from 1 to 4, said U, Wp and Xr substitution being sufficient to provide said radical with a non-coplanar molecular configuration; and

35
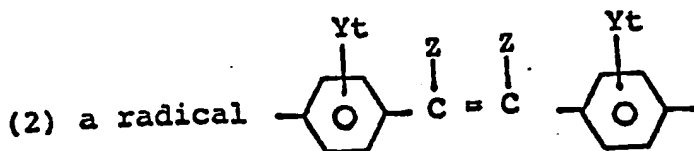
1

(2) a radical

$$-\bigⓄ-\overset{\overset{\displaystyle Z}{|}}{C}=\overset{\overset{\displaystyle Z}{|}}{C}-\bigⓄ-$$

where each of Y and Z is hydrogen or a substituent other
than hydrogen and each t is an integer from 1 to 4, with
the proviso that when each said Z is hydrogen, at least
one said Y substituent is a substituent other than hydrogen
positioned on the corresponding nucleus ortho with respect

10   to the $-\overset{\overset{\displaystyle Z}{|}}{C}=$ moiety of said radical, said Z and Yt substit-
ution being sufficient to provide said radical with a non-
coplanar molecular configuration;
and wherein, when c is zero, A is a divalent radical select-

15   ed from the group consisting of radicals (1) and (2) as
hereinbefore defined.

7.   A device according to claim 6 wherein c of said re-
curring units is the integer one.

20

8.   A device according to claims 6 or 7 wherein each said
radical (1) is a divalent radical having the formula

25

$$-\bigⓄ\overset{\displaystyle U}{\underset{\displaystyle X}{\bigⓄ}}-$$
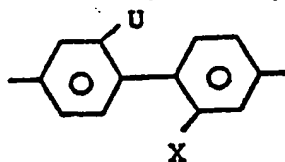
wherein each of U and X is a substituent other than

30   hydrogen.

9.   A device according to claim 8 wherein each of said U
and X substituents is selected from the group consisting of
halogen, nitro, alkoxy and substituted-alkyl.

35

10.   A device according to claims 6 to 9 wherein each of said A and B radicals of said recurring units is said divalent radical (1).

11.   A device according to claim 10 wherein said divalent radical A is a radical having the formula (1).
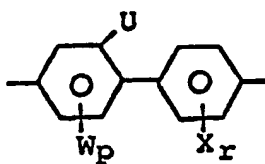
wherein p is the integer 3, r is the integer 4 and each of U, W and X is a substituent other than hydrogen, preferably a halogen such as fluoro.

12.   A device according to claim 10 wherein said divalent radical A is a radical having the formula
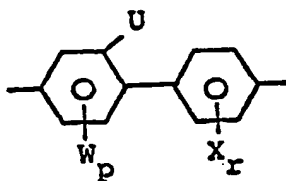
wherein p is the integer 3, r is the integer 4 and each of U, W and X is a substituent other than hydrogen; and said divalent radical B is a radical having the formula
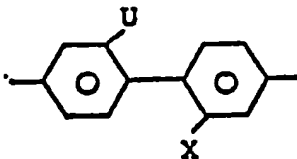
wherein each of U and X is a substituent other than hydrogen.

13. A device according to claims 6 or 7 wherein said divalent radical A is the radical having the formula
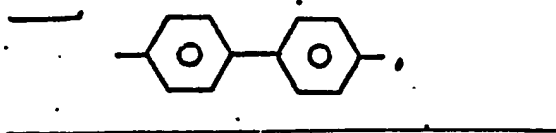
14. A device according to claim 7 wherein said B represents a single bond.

15. A device according to claim 7 wherein said divalent radical A is the radical having the formula

$$-\overset{\overset{\displaystyle CH_3}{|}}{C} = CH - CH = \overset{\overset{\displaystyle }{|}}{\underset{\displaystyle CH_3}{C}} - \;.$$
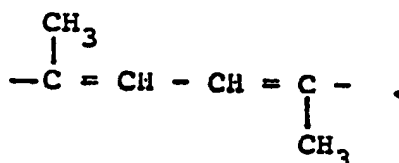
16. The device of claim 7 wherein said divalent radical A is the radical having the formula
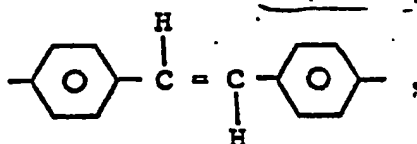
17. A device according to claim 7 wherein at least one of said A and B radicals is said divalent radical having the formula
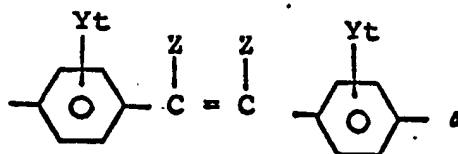
18. A device according to claim 17 wherein Z is hydrogen, and t is the integer one.

19. A device according to claim 18 wherein said Y sub-
stituent is selected from the group consisting of halogen,
nitro and alkoxy.

20. A device according to claim 17 wherein each Y is
hydrogen, each t is the integer four, one said Z is
hydrogen and the remaining said Z substituent is halogen.

21. A device according to claim 6 wherein c is zero.

22. A device according to claim 7 wherein said divalent
radical A is the radical having the formula

; and

said divalent radical B is a substituted-quaterphenylene
radical having the formula
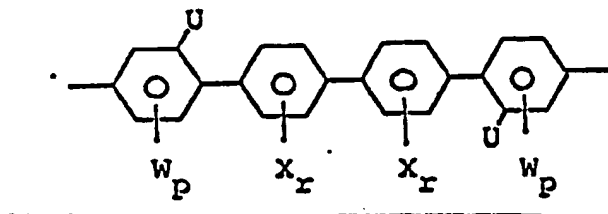
wherein each U is a substituent other than hydrogen, each
W is hydrogen or a substituent other than hydrogen, each p
is an integer from 1 to 3, each X is hydrogen or a sub-
stituent other than hydrogen and each r is an integer from
1 to 4, said U, W_p and X_r substitution being sufficient to
provide said radical with a non-coplanar molecular con-
figuration.

23. A device according to claim 7 wherein said divalent
radical A ist the radical having the formula

1 ation of bond and group polarizabilities of a repeating unit
of a polymer. It will be appreciated that electron density
distribution about axis X will be variously treated as a
cylindrical or ellipsoidal distribution depending upon the
relative magnitudes of the Y and Z vectors. In Fig. 4a is
5 shown an ellipsoidal cross-section along the axis of Fig. 3
where the magnitude of the shown Y vector is greater than
that of the Z vector. Ideally, Y and Z vectors would be
equal and the resulting circular cross-sectional distribut-
ion along the X axis is shown in Fig. 4b.
10

By a combination of longitudinal eccentricity (e_L) and
transverse eccentricity (e_T), based upon bond and group
polarizabilities, and the length and mean diameter of a
repeating unit, a geometric index, G, related to optical
15 anisotropy or birefringence, can be represented as follows:

$$G = 0.222 \left(\frac{1 + e_L}{1 + e_T} \right) \frac{L}{D}$$

20

wherein e_L, e_T, L and D have the meanings hereinbefore
ascribed. Longitudinal eccentricity e_L may be represented
according to the following relationship

25

$$e_L = \frac{\sqrt{X^2 - \frac{(Y + Z^2)}{2}}}{X}$$

Transverse eccentricity e_T may be represented by the
30 relationship

$$e_T = \frac{\sqrt{Y^2 - Z^2}}{Y}$$

35

1 wherein the magnitude of vector Y is the larger of the Y and Z vectors. Ideally, transverse eccentricity e_T will equal zero and longitudinal eccentricty e_L will equal one, in which case, eccentricity factor, E, will equal the theoretical maximum of two.

5

Geometric index G can be calculated for a variety of repeating units of a polymer material by resort to mean diameter and length values and longitudinal and transverse eccentricity values calculated from experimentally determined

10 dihedral angles. It will be appreciated that the magnitude of values of length, mean diameter, longitudinal eccentricity and transverse eccentricity will materially influence the value of geometric index G. Thus, it will be appreciated that a repeating unit having, for example, a length of

15 about twice that of a repeating unit having a different molecular structure and configuration will have a geometric index of about twice that of such different repeating unit. Accordingly, in making comparisons of geometric indices and magnitude thereof in relation to structural differences

20 between comparative molecular repeating units, such differences in length should be borne in mind.

In general, experimentally determined values of birefringence for polymeric materials comprised of repeating units as

25 aforedescribed will correlate directionally with values of geometric index, G, of the repeating units. Thus, in general, recurring units having higher geometric index values provide polymers exhibiting higher birefringence. Polymeric materials comprised of repeating units having a geometric index value,

30 G, of about 0.5 or higher exhibit high brefringence and can be utilized in the optical devices of the present invention. It will be preferred, however, that polymeric materials comprising repeating units having geometric index values of one or higher be utilized herein. Especially preferred

35 herein are polymers comprising repeating units of geometric

1   transparent layers, each said additional transparent layer
having an index of refraction substantially matching one
of the two indices of refraction of each said layer of
said molecularly oriented highly birefringent polymer.

5   30.   A multilayer device according to claim 29 wherein
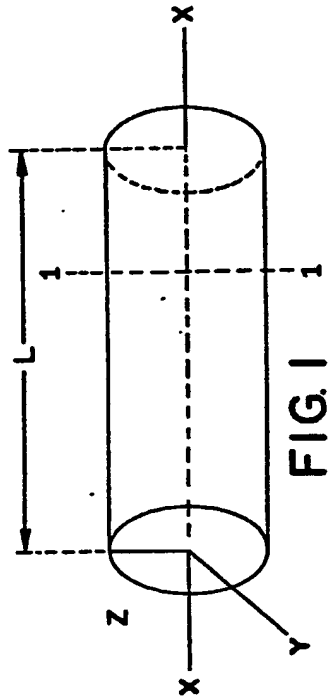each said additional transparent layer is isotropic.

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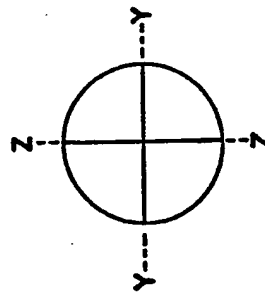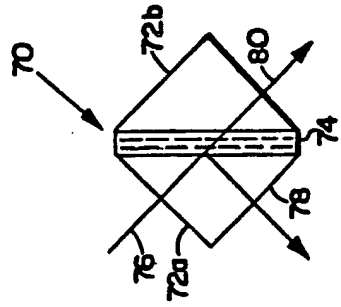FIG. 8

FIG. 4b

FIG. 2
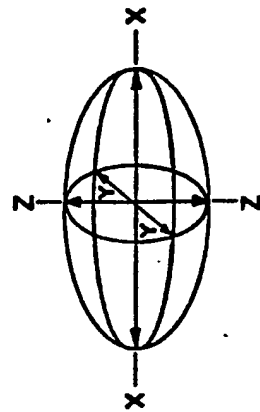
FIG. 4a

FIG. 1

FIG. 3

FIG. 5

FIG. 6

FIG. 7

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with Indication, where appropriate, of relevant passages	Relevant to claim
Y	US - A - 2 451 695 (R.S. SCHREIBER) * claims 1, 5 to 7 * —	1,6
Y	GB - A - 1 011 836 (INTERNATIONAL POLA-ROID CORP.) * claims 1, 7, 9 * —	1,6
A	US - A - 3 801 528 (P.W. MORGAN) * claims; column 4, lines 35, 36 * —	6,17
A	Chemical Abstracts vol. 88 no. 4 23 January 1978 Columbus, Ohio, USA A.V. SIDOROVICH et al. "Quasicrystalline state of aromatic heterocyclic polymers with imide rings" page 9, column 2, abstract no. 23545n & Dokl. Akad. Nauk.SSSR vol. 237, no. 1 1977, pages 156 to 159 —	
D,Y	US - A - 3 610 729 (H.G. ROGERS) * claim 1; column 2, lines 50 to 65; fig. * —	1,5, ·29,30
D,Y	US - A - 3 522 984 (H.G. ROGERS) * column 3, lines 62 to 74 * — ./..	1,5

CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)

G 02 B 1/08
C 08 G 69/32

TECHNICAL FIELDS SEARCHED (Int.Cl. 3)

C 08 G 69/00
G 02 B 1/08
G 02 B 5/30

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same category
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: earlier patent document, but published on, or after the filing date
D: document cited in the application
L: document cited for other reasons

&: member of the same patent family, corresponding document

X	The present search report has been drawn up for all claims		
Place of search ·Berlin	Date of completion of the search 11-05-1982	Examiner HASS/FUCHS	

European Patent Office

EUROPEAN SEARCH REPORT

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
D,Y	<u>US - A - 3 213 753</u> (H.G. ROGERS) * column 3, lines 8 to 28; column 9, line 74 to column 10, line 14 * —	25-28
A	<u>DE - C - 732 790</u> (H. SCHNEIDER AG) * claim 1 * —	1,5
A	<u>US - A - 2 748 659</u> (W. GEFFCKEN et al.) * fig. 1 * ——	

CLASSIFICATION OF THE APPLICATION (Int. Cl.³)

TECHNICAL FIELDS SEARCHED (Int. Cl.³)

EPO Form 1503.2 08.78